

Practical Spectroscopy:

The Rapid Interpretation of Spectral Data

for McMurry's *Organic Chemistry*, 5e



Paul R. Young

Organic Chemistry *Online*
Spectroscopy Supplement

Practical Spectroscopy
***The Rapid Interpretation of
Spectral Data***

Paul R. Young
Department of Chemistry
University of Illinois at Chicago

Senior Assistant Editor: *Melissa D. Henderson*
Editorial Assistant: *Dena Dowsett-Jones*
Marketing Manager: *Steve Catalano*
Marketing Assistant: *Christina De Veto*
Production Coordinator: *Dorothy Bell*

Cover Design: *Vernon T. Boes*
Cover Photo: © *J. Jansen, Natural Selection*
Manufacturing Buyer: *Nancy Panziera*
Printing and Binding: *Globus Printing*

COPYRIGHT © 2000 by Brooks/Cole
A division of Thomson Learning
The Thomson Learning logo is a trademark used herein under license.

For more information, contact:
BROOKS/COLE
511 Forest Lodge Road
Pacific Grove, CA 93950 USA
www.brookscole.com

All rights reserved. No part of this work may be reproduced, transcribed or used in any form or by any means—graphic, electronic, or mechanical, including photocopying, recording, taping, Web distribution, or information storage and/or retrieval systems—without the prior written permission of the publisher.

For permission to use material from this work, contact us by
web: www.thomsonrights.com
fax: 1-800-730-2215
phone: 1-800-730-2214

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

ISBN 0-534-37230-9

Contents

Chapter 1 Molecular Formulas and Degrees of Unsaturation	1
Calculating <i>Degrees of Unsaturation</i> from the Molecular Formula	2
Chapter 2 Mass Spectrometry	7
Fragmentation Patterns of Common Functional Groups	10
Aliphatic Compounds	10
Alcohols and Phenols	12
Aldehydes and Ketones	14
Alkenes and Alkynes	17
Amines	18
Aromatic Hydrocarbons	20
Carboxylate Esters and Carboxylic Acids	21
Ethers	23
Nitriles and Amides	24
Other Techniques for Ionization	25
Field Ionization	25
Chemical Ionization	26
Summary of Useful Information	26
Chapter 3 Infrared Spectroscopy	29
Obtaining Infrared Spectra	29
Symmetry Considerations in Infrared Spectroscopy	30
Infrared Spectroscopy and the Organic Chemist	32
The Interpretation of Infrared Spectra	32
Region 1: the O-H and N-H Stretch	32
Region 2: the <i>sp</i> and <i>sp</i> ² C-H Stretch	34
Region 3: the <i>sp</i> ³ C-H Stretch	35
Region 4: the Aldehyde <i>sp</i> ² C-H Stretch	35
Region 5: the Nitrile C≡N and Alkyne C≡C Stretch	36
Region 6: the Carbonyl C=O Stretch	36
Region 7: the C=C Stretch	38
Region 8: the <i>Fingerprint Region</i>	39
Chapter 4 Nuclear Magnetic Resonance Spectroscopy	41
Nuclear Magnetic Resonance Spectrometers	43
The Continuous Wave Spectrometer	43
The Pulsed Fourier Transform Spectrometer	44
Proton NMR	44
Integration: Relative Signal Intensities	44
Chemical Shifts	45
Spin Coupling	46
The Coupling Constant	49
Magnetic Anisotropy	50
Carbon NMR	51
Chemical Shifts	51
Spin Coupling	52
Proton-Decoupled ¹³ C NMR Spectra	52
Problems with Integration in ¹³ C NMR	53
Chapter 5 Integrated Spectroscopy Problems	55
The Mass Spectrum	55
The Analysis	56
The Infrared Spectrum	56
The ¹H NMR Spectrum	56
The ¹³C NMR Spectrum	57
The Integrated Spectroscopy Problem Sets: 1 - 100	59-158

Chapter 1

MOLECULAR FORMULAS AND DEGREES OF UNSATURATION

The classical method for determining a molecular formula is combustion analysis. A small amount of the compound (1–2 mg) is carefully weighed, and is burned in pure oxygen. The water and carbon dioxide produced are collected and the change in weight carefully determined. Knowing the stoichiometry of the combustion process and all of the weights, the percentage composition of carbon and hydrogen can be determined.

Today, commercial analytical laboratories perform combustion analyses quickly and accurately using gas chromatographs with thermal conductivity detectors. A routine analysis will give the percentage composition of carbon, hydrogen, and nitrogen. Oxygen is difficult to determine, and is generally calculated by difference; analyses for other atoms are also available by special request.

In the Problems section of this book (Chapter 5), percent compositions are provided for carbon, hydrogen, nitrogen and oxygen. Halogens are omitted, because identifying the halogen (and its stoichiometry) constitutes an interesting exercise in mass spectrometry, and so halogen content (once it is established) should be calculated by difference in these problems.

The process of molecular formula calculation allows you to re-visit the good old days of general chemistry. The general procedure is as follows:

The percentage of each element should be converted into molar units. This is accomplished by dividing the percentage composition by the molecular weight.

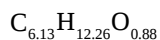
For a 100 gram sample with an analysis of 73.63% C, 12.36% H, and 14.01% O;

$$\text{moles of carbon} = (73.63 \text{ g}) / (12.01 \text{ g / mole}) = 6.13,$$

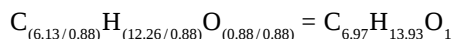
$$\text{moles of hydrogen} = (12.36 \text{ g}) / (1.008 \text{ g / mole}) = 12.26,$$

$$\text{moles of oxygen} = (14.01 \text{ g}) / (16.0 \text{ g / mole}) = 0.876,$$

giving the result,



We typically don't deal with compounds with non-integer stoichiometry, so these should be converted into the simplest whole number ratio:



which is rounded to give,



The formula obtained is the empirical formula and represents the whole-number ratio of the elements

in the compound. For cyclohexane, C_6H_{12} , the **empirical formula** is CH_2 ; in order to convert this to the molecular formula, you need to know the molecular weight of the compound.

While there are classical methods for the determination of molecular weights, the most contemporary method (and the one utilized in this book) is mass spectrometry. The mass spectrum of cyclohexane shows a molecular ion at $m/e = 84$, telling you that there must be six CH_2 units (weighing 14 amu each) in the molecular formula.

Another example:

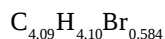
A 100-gram sample has an analysis of 49.16% C, 4.13% H, and the compound contains halogen. The mass spectrum for this compound shows two molecular ions at $m/e = 170$ and 172 of equal intensity, with a fragmentation of $(m_{\text{average}} - 80) = 91$. From the fact that two molecular ions of equal intensity are observed, along with the $(m_{\text{average}} - 80)$ peak, the compound is concluded to contain bromine (bromine consists of approximately equal concentrations of ^{79}Br and ^{81}Br ; see **Chapter 3** for more details on isotopic ratios). Therefore the percentage of bromine must be $(100 - (49.16 + 4.13)) = 46.71$.

$$\text{moles of carbon} = (49.16 \text{ g}) / (12.01 \text{ g / mole}) = 4.09,$$

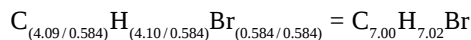
$$\text{moles of hydrogen} = (4.13 \text{ g}) / (1.008 \text{ g / mole}) = 4.10,$$

$$\text{moles of bromine} = (46.71 \text{ g}) / (80.0 \text{ g / mole}) = 0.584,$$

giving the result,



Converting into the simplest whole number ratio:



which is rounded to give,



Calculating Degrees of Unsaturation from the Molecular Formula

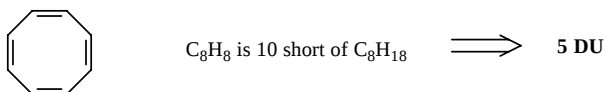
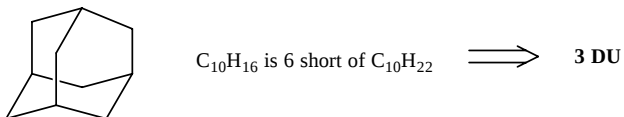
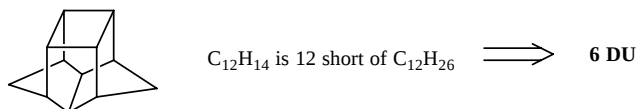
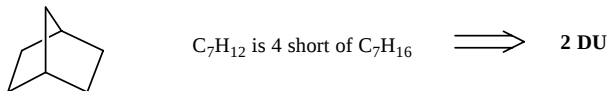
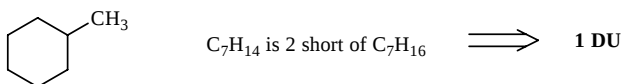
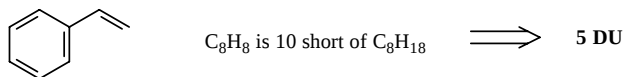
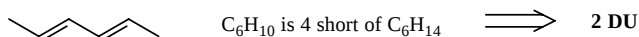
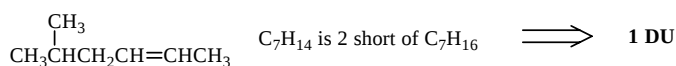
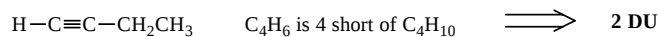
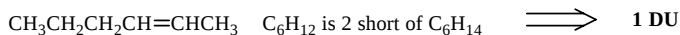
The general formula for an alkane is given by $2n + 2$ where n is the number of carbons in the molecule. Cycloalkanes and alkenes, however, have two fewer hydrogens than the corresponding parent hydrocarbon. For example, ethene ($H_2C=CH_2$) has the molecular formula C_2H_4 and ethane (CH_3CH_3) has the formula C_2H_6 (following the $2n + 2$ rule). In cycloalkanes, two of the valences are utilized to close the ring; cyclohexane is C_6H_{12} , while hexane is C_6H_{14} .

Knowing this relationship, it is possible to take a molecular formula and calculate the **degree of unsaturation**; that is, the **total number of multiple bonds or rings in a molecule**. This information can then be utilized in the conversion of analytical data into structural possibilities.

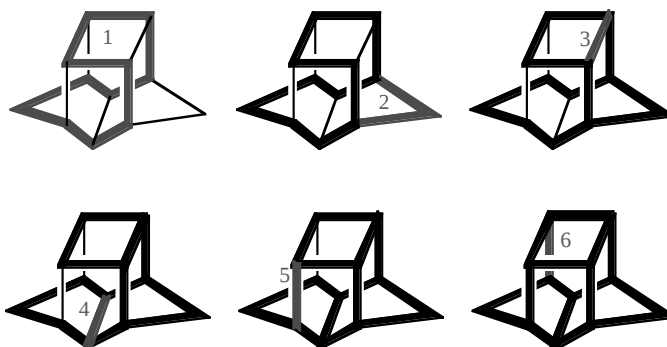
For hydrocarbons, the process is simple:

- Take the parent hydrocarbon and calculate the number of hydrogens using the $2n + 2$ rule,
- Every **two hydrogens** that are “missing” in the analysis of the unknown represent one **degree of unsaturation**. When counting rings in a polycyclic compound, you are not allowed to *retrace* any path, only to connect atoms to the parent ring by following **new paths**. An example of this exercise is shown below. It is also possible (and often easier) simply to examine most compounds and *count* the number of rings and multiple bonds to determine the *unsaturation number*.

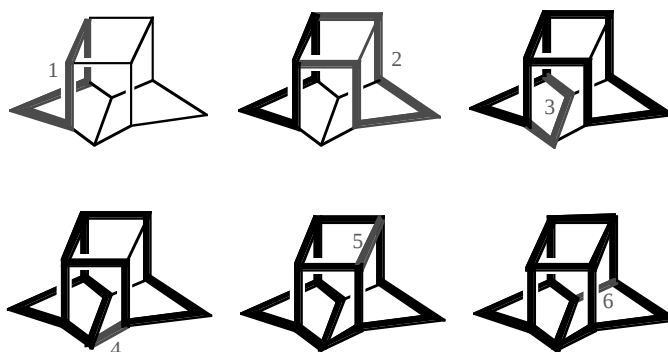
Some simple examples:



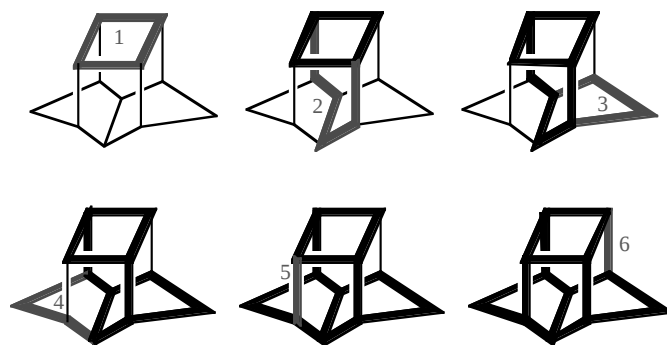
Calculating degrees of unsaturation in complex polycyclic compounds can be difficult. Compound 8 in the preceding examples has a molecular formula of $\text{C}_{12}\text{H}_{14}$, and by the simple calculation, must have six degrees of unsaturation. Visualizing six rings in the compound, however, is not trivial. In order to identify the rings in a structure such as this, you should begin by tracing any complete ring of carbons (or heteroatoms) in the polycyclic ring structure (generally the largest ring, but this is not required); this is ring #1. Next connect the remaining ring atoms to the parent ring, by any path, but being careful not to retrace any paths previously used. Finally, connect any remaining segments by the longest path available, again, being careful not to retrace. Three possible sequences for Compound 8 follow:



Starting on one side...



...or, starting on the top...



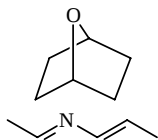
For compounds containing elements other than carbon and hydrogen, degrees of unsaturation can be calculated as follows:

Organohalogen compounds: because a halogen is simply a replacement for a hydrogen in an organic molecule (a valence of one), you simply **add the total number of halogens** to the carbon-hydrogen analysis, and calculate the unsaturation number as described above.

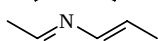
Organooxygen compounds: because oxygen is divalent, it has *no effect* on the calculation for the degree of unsaturation, and can be simply ignored. This can be demonstrated by considering ethanol ($\text{CH}_3\text{CH}_2\text{OH}$); removing the oxygen produces ethane ($\text{CH}_3\text{CH}_2\text{-H}$). The calculation for ethanol (ignoring the oxygen) therefore gives *no degrees of unsaturation*. For a carbonyl, (i.e., acetone, CH_3COCH_3), ignoring the oxygen gives C_3H_6 , two hydrogens short of $(2n + 2)$, and one degree of unsaturation. The carbonyl is therefore equivalent to one degree of unsaturation.

Organonitrogen compounds: because nitrogen is trivalent, an organonitrogen compound has *one more* hydrogen than an equivalent hydrocarbon has, and therefore you should ignore the nitrogen and **subtract the number of nitrogens from the total number of hydrogens** and calculate as described above.

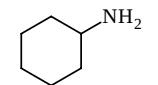
Some examples:



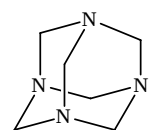
$$\text{C}_6\text{H}_{10}\text{O} \implies \text{"C}_6\text{H}_{10}\text{" which is 4 short of C}_7\text{H}_{16} \implies \mathbf{2 \text{ DU}}$$



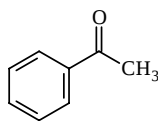
$$\text{C}_5\text{H}_9\text{N} \implies \text{"C}_5\text{H}_8\text{" which is 2 short of C}_7\text{H}_{16} \implies \mathbf{2 \text{ DU}}$$



$$\text{C}_6\text{H}_{15}\text{N} \implies \text{"C}_6\text{H}_{12}\text{" which is 12 short of C}_{12}\text{H}_{26} \implies \mathbf{1 \text{ DU}}$$



$$\text{C}_6\text{H}_{13}\text{N}_4 \implies \text{"C}_6\text{H}_8\text{" which is 4 short of C}_{10}\text{H}_{22} \implies \mathbf{3 \text{ DU}}$$



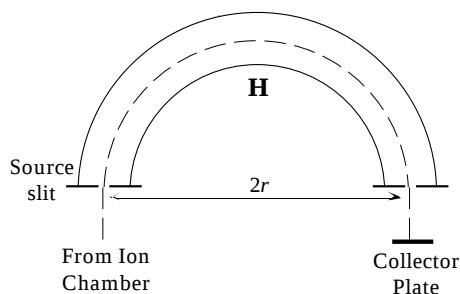
$$\text{C}_8\text{H}_8\text{O} \implies \text{"C}_8\text{H}_8\text{" which is 10 short of C}_8\text{H}_{18} \implies \mathbf{5 \text{ DU}}$$

Chapter 2

MASS SPECTROMETRY

The **mass spectrometer** is an instrument that utilizes a variety of methods to ionize organic and biological compounds into simple cations and cationic species containing one unpaired electron (**cation radicals**). Typically, these ions are accelerated in an electric field and separated in a magnetic analyzer according to their **mass-to-charge ratio** (m/z or m/e ratio). Because the charge on these ions is typically +1, the mass-to-charge ratio provides a direct measure of the **molecular weight** of the cation or cation radical species.

In the simplest form of the instrument, the energy required to effect ionization is provided by an electron beam with an energy of 10 to 70 eV (1 eV $\cong$ 23 kcal/mol $\cong$ 96 kJ/mol). In this design, the compound is introduced as a vapor into a very high vacuum. A *molecular leak* from the sample chamber allows a dilute stream of molecules in the gas phase to interact with the electron beam, where ionization occurs. The ions are then accelerated and analyzed. A schematic of a simple *magnetic analyzer* is shown below.



Within the analyzer, ions are subjected to a centripetal acceleration by the magnetic field, **H**, which results in the ion being deflected along a circular path of radius r . The radius of the path is a function of the mass-to-charge ratio of the ion, (m/z) the magnetic field strength, **H**, and the accelerating potential, V , as described by the equation given below.

$$r = \sqrt{\frac{2V(m/z)}{H^2}}$$

Thus, for a given ion, the radial path within the analyzer is a simple function of both the magnetic field strength and the accelerating voltage, and either of these can be adjusted so that an ion of a given mass-to-charge ratio traverses the center of the analyzer and impacts on the collector plate. In practice, either the field strength or the accelerating voltage are continuously varied so that the desired range of masses are covered. The output from the detector circuitry over this range comprises the *mass spectrum*.

With modern instrumentation, the data from a mass spectrum are collected by a host computer and output in the form of *relative peak intensity* as a function of *mass-to-charge ratio*. The peak intensities are normalized as a percentage of the most intense peak in the spectrum (the **base peak**), and the spectrum appears as a *bar graph* with intensities separated by single mass units (**Figure 2.1**).

The lowest energy ionization that occurs in the electron beam is loss of an electron from the highest occupied molecular orbital of the molecule, that is, the ionization potential of the molecule (the I.P.). This process typically requires 10 eV or less and results in the formation of a cation radical which is termed the molecular ion (M^+ or m^+). The molecular ion is useful because it provides the molecular weight of the molecule and can also provide information regarding the halogen content. This is because chlorine and bromine exist as easily identified isotopic mixtures. Chlorine (average molecular weight 35.5) consists of ^{35}Cl and ^{37}Cl in a ratio of approximately 3 : 1 (see **Table 2-1**) while bromine (average molecular weight 80) consists of ^{79}Br and ^{81}Br in essentially equal concentrations. That means a compound containing chlorine will display two molecular ions, two mass units apart, (one arising from ^{35}Cl and one from ^{37}Cl) in the ratio of 3 : 1. Likewise a compound with a single bromine will have two molecular ions, two mass units apart, in the ratio of 1 : 1. More complex mixtures of these two halogens give recognizable patterns, as shown in **Table 2-2**.

If the electron which interacts with a given gas-phase molecule has sufficient energy (generally 50-70 eV), the ion which is formed can undergo fragmentation reactions. These reactions can include loss of hydrogen atoms, alkyl groups, alkoxy groups, elimination reactions, rearrangements, etc., and each of these reaction pathways will possess a unique activation energy. In general, the ion will partition by these various pathways as a simple function of the activation energy of each pathway. An example of this type of partitioning is given by the mass spectrum of methyl 2-methylbenzoate (**Figure 2.1**).

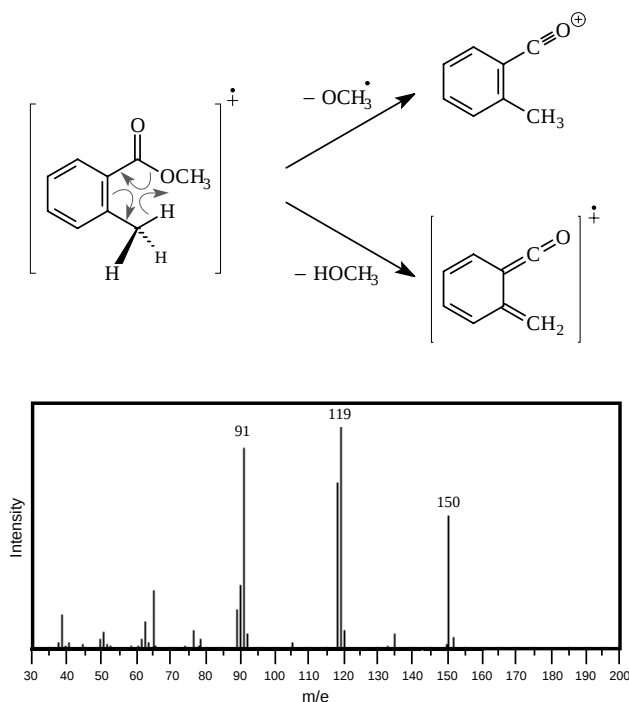


Figure 2.1 Mass spectrum of methyl 2-methylbenzoate.

The molecular weight of the compound is 150 and the molecular ion appears as a peak which is roughly 60% of the base peak. The small peaks at $M + 1$ and $M + 2$ represent the minor isotopic abundance of ^{13}C and ^{18}O . The base peak in the spectrum at $m/z = 119$ represents loss of 31 mass units from the molecular ion and corresponds to the loss of a methoxy radical to form the 2-methylbenzoyl cation. The less intense peak at $m/z = 118$ corresponds to loss of neutral methanol from the base peak to give the cation-radical shown in the Scheme. Loss of methanol requires a cyclic mechanism in which the methyl group donates a hydrogen to the methoxyl group, concurrent with the cleavage of the carbon-oxygen bond. This process has a higher activation energy due to the entropic requirement of attaining the correct geometry for the reaction to occur, hence the process is less probable and the intensity of the fragment is less.

In general, ions that form from primary fragmentation have sufficient energy to fragment further. Thus, in the previous Scheme, the ion formed by the loss of methoxy radical can undergo further cleavage to lose carbon monoxide, giving an ion with $m/z = 91$ (90% intensity, relative to the base peak). While it is tempting to say that the stability of an ion dictates its abundance in the mass spectrum, you should remember that ions in the mass spectrum result from **kinetically controlled reactions**, not thermodynamic stability. Hammond Postulate effects generally dictate that stable ions will form more rapidly, with the notable exception that high-entropy processes will always be disfavored.

The following simple conclusions should be evident from the above discussion:

- The **molecular ion** provides the molecular weight of the compound and may provide information regarding halogen (chlorine and bromine) content. Highly intense molecular ions will be observed when pathways for fragmentation of the molecular ion involve high-energy processes.
- The **base peak** of a mass spectrum (other than M^+) corresponds to the lowest energy cleavage pathway of the molecular ion and may represent the most stable cation (or cation-radical) fragment of the molecule.
- Whenever there are two or more competing pathways for fragmentation of a precursor ion, **the lowest activation energy process will generally predominate**.

Table 2-1

Atomic weights and approximate natural abundance of common isotopes.

Isotope	Atomic Weight	Natural Abundance (%)
^1H	1.007825	99.985
^2H	2.014102	0.015
^{12}C	12.000000	98.0
^{13}C	13.003354	1.1
^{14}N	14.003074	99.64
^{15}N	15.000108	0.36
^{16}O	15.994915	99.8
^{17}O	16.999133	0.04
^{18}O	17.999160	0.2
^{19}F	18.998405	100
^{31}P	30.973763	100
^{35}Cl	34.968855	75.8
^{37}Cl	36.965896	24.2
^{79}Br	78.918348	50.5
^{81}Br	80.916344	49.5
^{127}I	126.904352	100

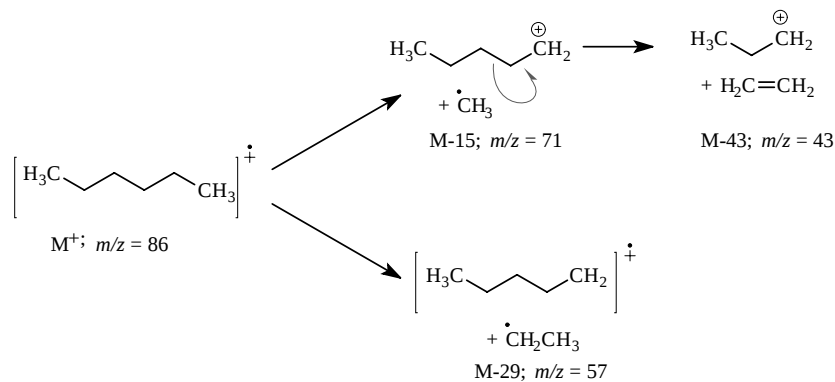
	Br	Br ₂	Br ₃
Relative Intensity			
	m/z	m/z	m/z
Relative Intensity			
	m/z	m/z	m/z
Relative Intensity			
	m/z	m/z	m/z

Table 2-2 Predicted ratios of molecular ions for compounds containing various ratios of chlorine and bromine, based on natural isotopic abundance.

Fragmentation Patterns of Common Functional Groups

Aliphatic Compounds

The mass spectrum of saturated hydrocarbons (**Figure 2.2**, hexane) generally consists of a number of even-electron ions formed by expulsion of a radical (often a methyl group) from the molecular ion, followed by loss of ethene due to the fission process shown below:



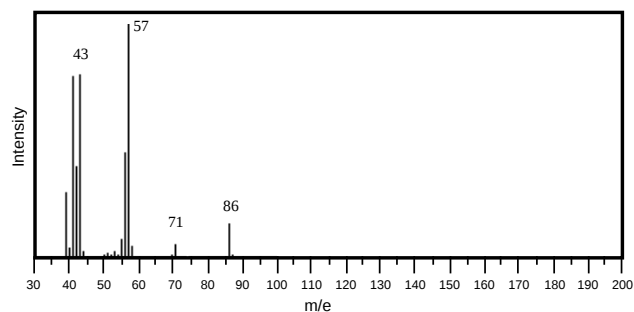
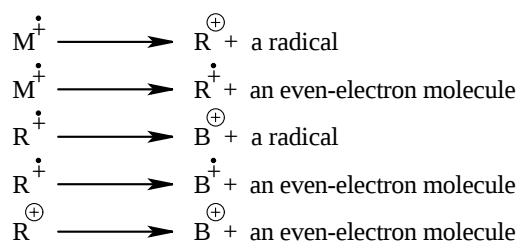


Figure 2.2 Mass spectrum of hexane.

This example also serves to demonstrate the **Even Electron Rule** for fragmentation of cations and cation-radicals; **odd electron ions decompose by loss of radicals or even electron molecules, while even-electron ions decompose by loss of even-electron molecules.** Summarizing:



As the carbon skeleton of an alkane becomes more highly branched, the intensity of the molecular ion generally decreases and the preferential cleavage is to form the more stable branched carbocation, as seen in the mass spectrum of 2-methylpropane (Figure 2.3).

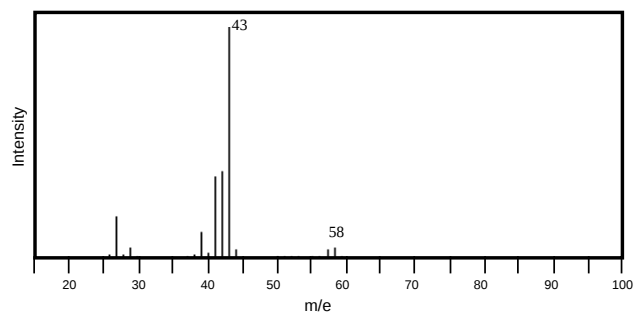
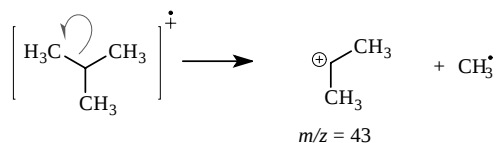


Figure 2.3 Mass spectrum of 2-methylpropane.

For this compound, the primary cleavage of the molecular ion is loss of a methyl radical to give the even-electron secondary carbocation. Tetra-substituted alkane carbons generally expel an alkane radical, to give tertiary carbocations (Figure 2.4, 2,2-dimethylpropane). In this spectrum, the molecular ion ($m/z = 72$) does not show, and the spectrum is dominated by the M-15 peak at $m/z = 57$, corresponding to loss of a methyl radical to give the *tert*-butyl carbocation.

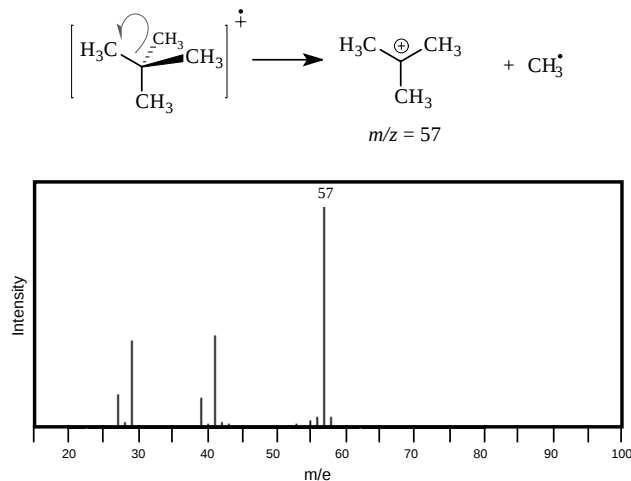


Figure 2.4 Mass spectrum of 2,2-dimethylpropane. The molecular ion at $m/e = 72$ does not show in this spectrum.

Alcohols and Phenols

Primary and secondary alcohols often form minor molecular ions, as shown by the mass spectrum of 2-butanol (**Figure 2.5**). At 70 eV, the molecular ion at $m/z = 74$ is barely visible, as is a weak M-1 peak. Loss of an alkyl group (usually the largest) as a radical gives the even-electron cation; for 2-butanol, this fragmentation is shown below.

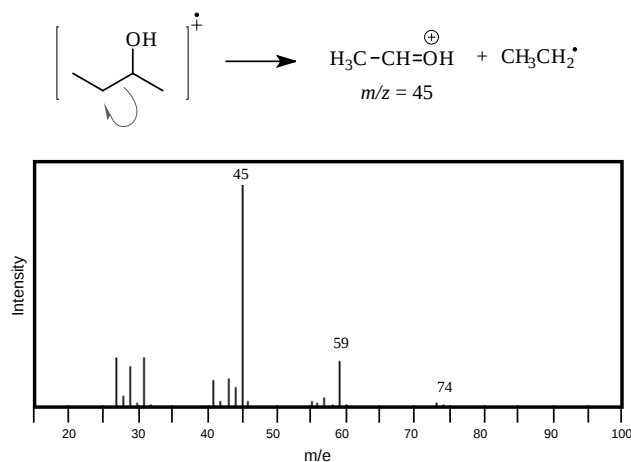
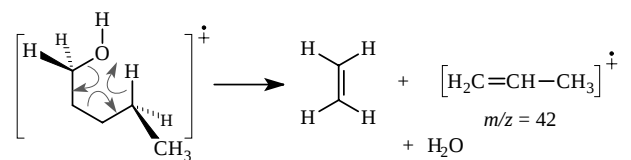


Figure 2.5 Mass spectrum of 2-butanol.

Dehydration ($M - 18$) is also a common fragmentation for long-chain alcohols, as shown for 1-pentanol (**Figure 2.6**). This spectrum also shows the ability of long-chain alcohols to undergo simultaneous loss of water and ethene by the cyclic mechanism shown below.



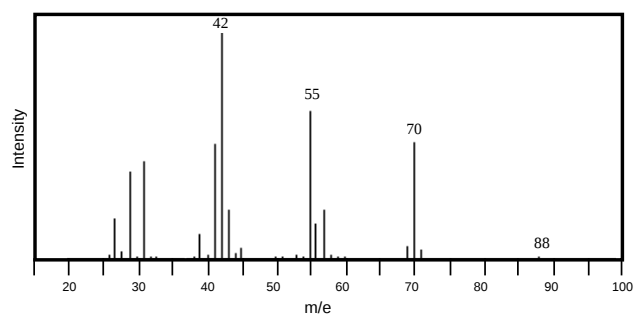


Figure 2.6 Mass spectrum of 1-pentanol.

Dehydration of the molecular ion from cyclohexanol results in the formation of bridged bicyclic cation radicals. The base peak corresponds to ring-opening adjacent to the alcohol carbon and loss of a propyl radical to give the even-electron cation at $m/z = 57$ (**Figure 2.7**).

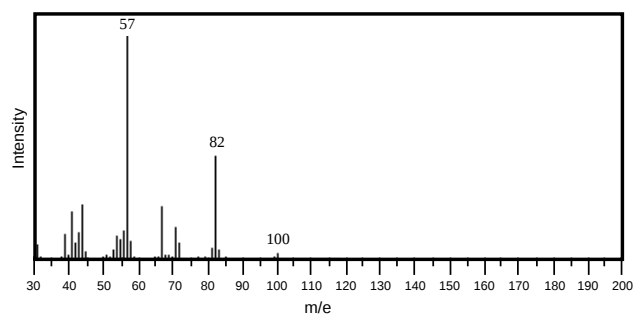
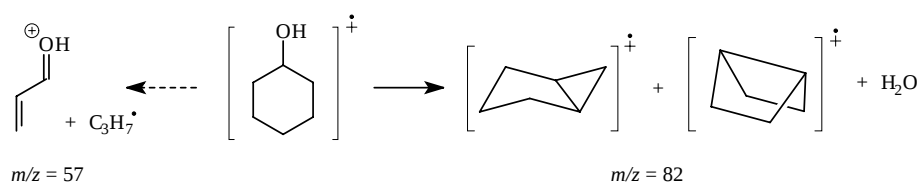


Figure 2.7 Mass spectrum of cyclohexanol.

Phenols typically give significant molecular ions and show major peaks for the loss of carbon monoxide ($M - 28$) and the formyl radical ($M - 29$), as shown for phenol, itself, in **Figure 2.8**.

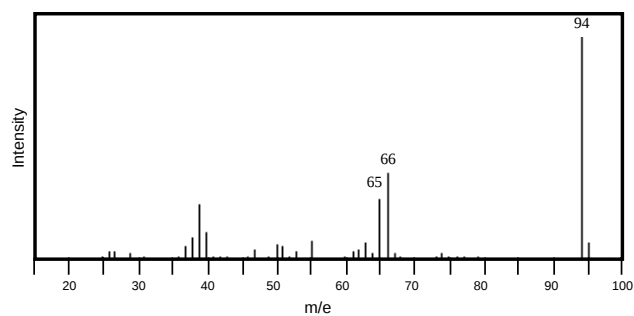


Figure 2.8 Mass spectrum of phenol.

Aldehydes and Ketones

Ketones and aldehydes generally undergo fragmentation by the α -cleavage of one of the groups attached to the carbonyl carbon to form the resonance-stabilized oxocarbenium ion. For aldehydes, this results in the loss of a hydrogen atom (M-1) or in the loss of an alkyl or aryl radical. For many aldehydes, the M-1 peak undergoes further fragmentation to give CO and an even-electron alkyl or aryl carbocation, and the importance of the M-1 peak in the spectrum depends on the exact nature of the substituents. For simple aldehydes (**Figure 2.9**, propanal) the M-1 fragmentation has an intensity of about 25% of the molecular ion ($m/z = 58$) with the base peak corresponding to the ethyl carbocation and the CHO cation (both M-29).

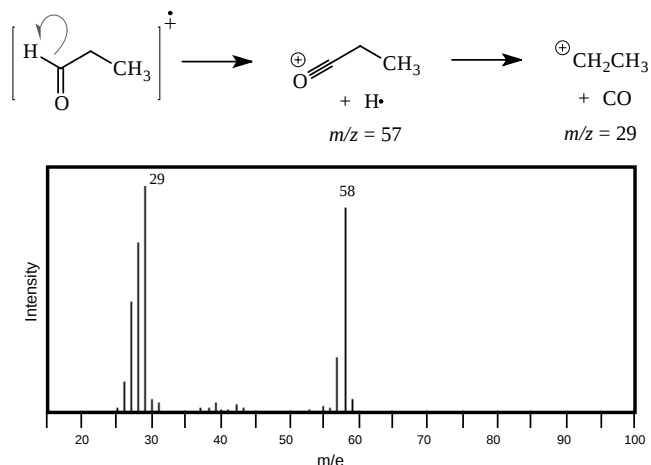


Figure 2.9 Mass spectrum of propanal.

For propenal (**Figure 2.10**), loss of CO to form the less-stable vinyl radical is higher energy and the M-1 peak ($m/z = 55$) is more significant.

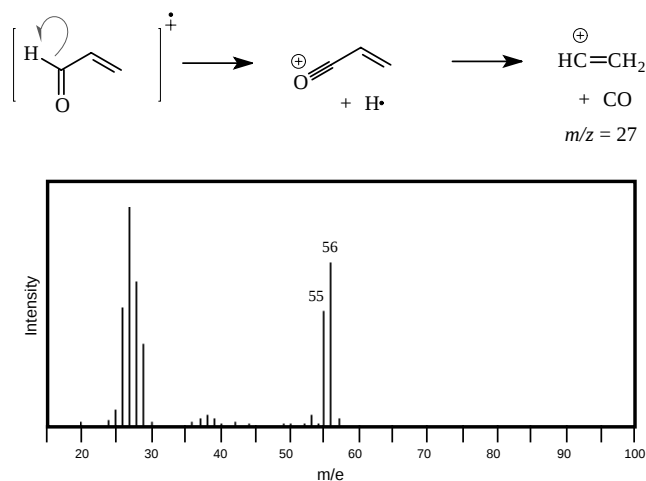


Figure 2.10 Mass spectrum of 2-propenal.

Neither the molecular ion nor the M-1 peak is significant in hexanal (**Figure 2.11**) where the primary fragments arise from loss of CO and fragmentation of the alkyl side-chain. The mass spectrum of hexanal also shows a major peak at $m/z = 44$ (the base peak) which is due to expulsion of neutral ethene from the molecular ion by a pathway known as the **McLafferty rearrangement**. This type of cyclic rearrangement occurs commonly in aliphatic aldehydes, ketones, acyl compounds, and in alkyl benzenes.

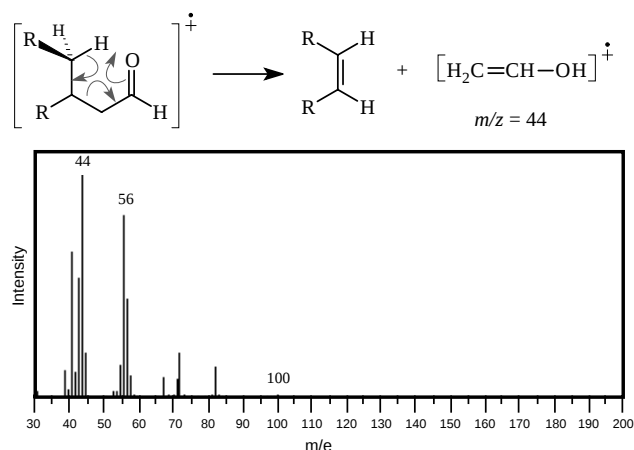
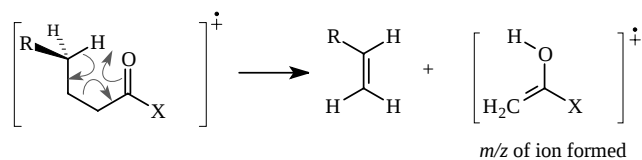


Figure 2.11 Mass spectrum of hexanal.

Other carbonyl compounds with alkyl chains containing three or more carbons also undergo the McLafferty rearrangement reaction and yield rearrangement ions with characteristic m/z values, as shown in the Table below.

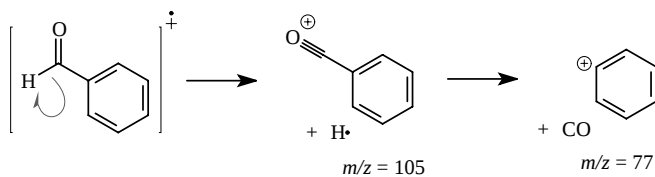
Table 2-3

Mass-to-charge ratios of McLafferty rearrangement ions for common carbonyl compounds.



Functional Group	X	m/z
Aldehyde	-H	44
Methyl Ketone	-CH ₃	58
Amide	-NH ₂	59
Carboxylic Acid	-OH	60
Ethyl Ketone	-CH ₂ CH ₃	72
Methyl Ester	-OCH ₃	74
Ethyl Ester	-OCH ₂ CH ₃	88

Aromatic aldehydes, such as benzaldehyde (**Figure 2.12**), typically display intense molecular ions and M-1 peaks. In the mass spectrum of benzaldehyde, the oxocarbenium ion formed by loss of a hydrogen atom, expels CO to give the phenyl cation, C₆H₅⁺ at $m/z = 77$.



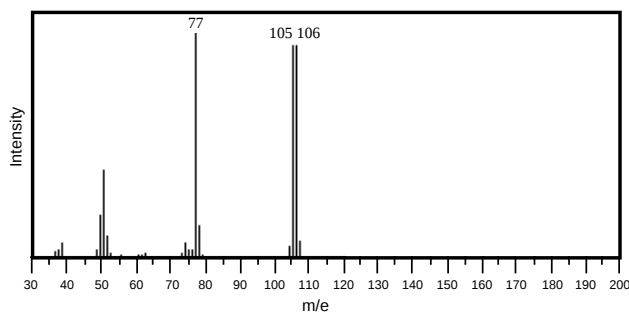


Figure 2.12 Mass spectrum of benzaldehyde.

Ketones fragment in a manner analogous to aldehydes, with α -cleavage being a predominant mechanism. In an unsymmetrical ketone, the *larger* alkyl group is more likely to be lost; thus in the mass spectrum of 2-butanone (Figure 2.13), α -cleavage to give the oxocarbenium ion at $m/z = 43$ (loss of the ethyl group) is more favorable than formation of the oxocarbenium ion at $m/z = 57$ (loss of the methyl group).

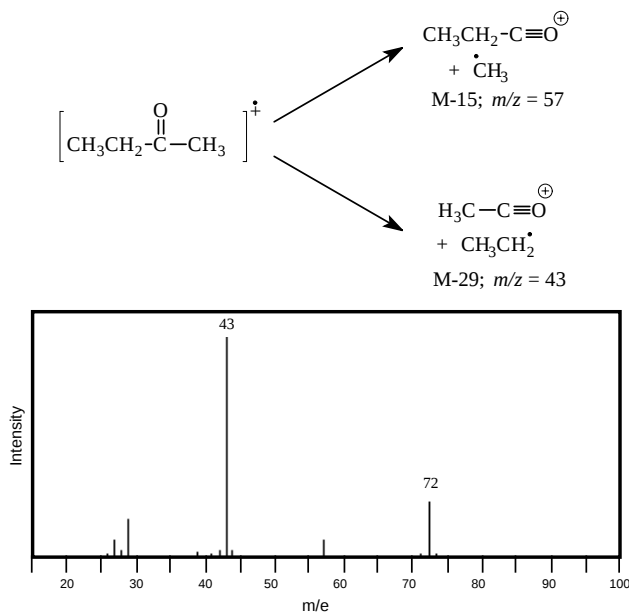
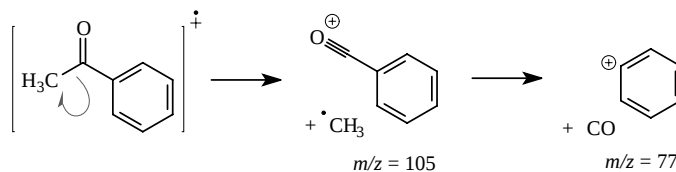


Figure 2.13 Mass spectrum of 2-butanone.

Aromatic ketones undergo α -cleavage to give phenyl oxocarbenium ions, which expel CO to produce the phenyl cation, C_6H_5^+ at $m/z = 77$. These peaks are evident in the spectrum of acetophenone (Figure 2.14), where the molecular ion at $m/z = 120$ fragments, with loss of a methyl radical to give the oxocarbenium ion at $m/z = 105$, and finally fragmenting again to form the phenyl cation at $m/z = 77$.



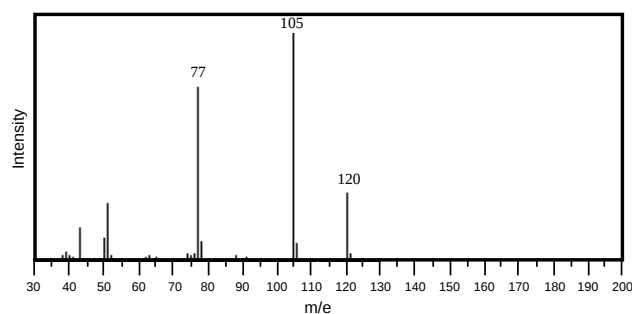


Figure 2.14 Mass spectrum of acetophenone.

Alkenes and Alkynes

Electron bombardment of the alkene π -system readily removes one electron to form a relatively stable cation radical, thus alkenes, in general, display a significant molecular ion in the mass spectrum. Other information regarding alkene structure and stereochemistry is, however, generally not available from the mass spectrum and it is not uncommon for structural isomers (i.e., 1- and 2-butene) to have virtually identical mass spectra.

In most simple (non-cyclic) alkenes, the base peak corresponds to the allyl cation ($m/z = 41$). In a terminal alkene, this is formed by β -cleavage of the molecular ion, as shown below. This ion also appears in non-terminal alkenes (for example, 2-butene, **Figure 2.15**), due to rapid rearrangements to form this stable ion.

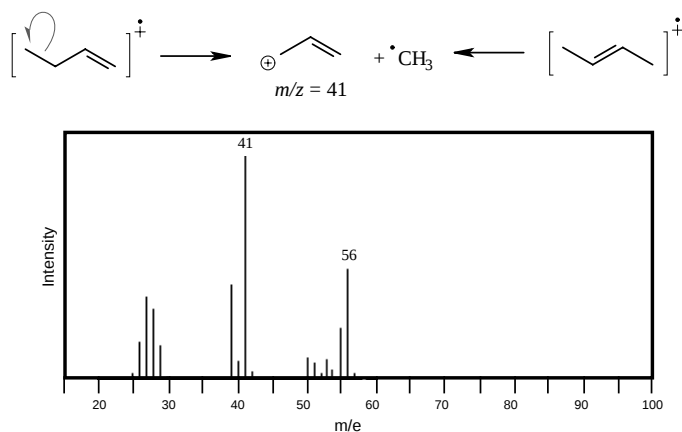
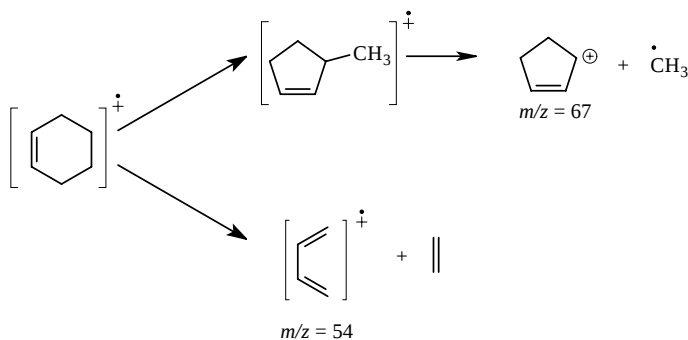


Figure 2.15 Mass spectrum of 2-butene.

The mass spectrum of cyclohexene (**Figure 2.16**) shows two common fragmentation reactions which are characteristic of cyclohexene rings; the base peak at $m/z = 67$, M-15 (rearrangement, then loss of a methyl) and loss of ethene at $m/z = 54$, M-26 (you should note that this is a **reverse Diels-Alder reaction**).



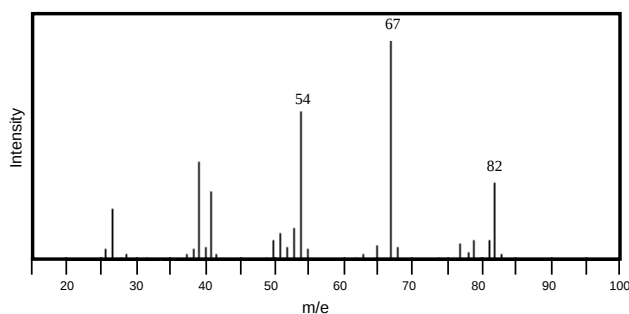


Figure 2.16 Mass spectrum of cyclohexene.

The behavior of alkynes in the mass spectrum is similar to that of alkenes, and little structural information is generally available. Terminal alkynes undergo a characteristic loss of a hydrogen atom to give intense M-1 peaks (Figure 2.17).

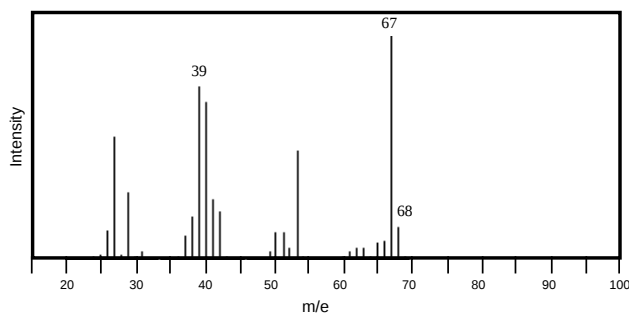


Figure 2.17 Mass spectrum of 1-pentyne.

Amines

Although nitrogen has an even atomic weight (^{14}N), it has an odd valence, thus, *if a molecule contains an odd number of nitrogen atoms, it must have an odd molecular weight*. Simple amines, amides, nitriles, and nitro compounds can be easily distinguished from simple carbon compounds (containing oxygen, sulfur, etc.) because their mass spectra will display odd-numbered molecular ions. Unfortunately, for many of these compounds, molecular ions are often weak or absent from the spectrum altogether.

The most intense peak in the mass spectrum of most simple aliphatic amines results from α -cleavage to give the immonium cation. For primary amines, this results in an intense peak at $m/z = 30$, as seen in the mass spectrum of propylamine (Figure 2.18).

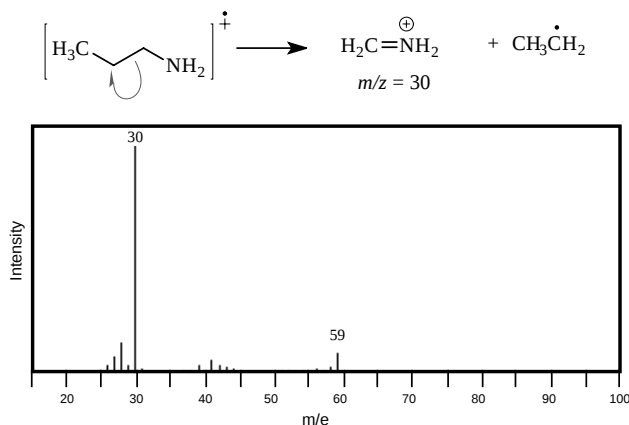


Figure 2.18 Mass spectrum of propylamine (propanamine).

For amines that are branched at the α -carbon, the larger of the alkyl groups is typically lost, as shown by the M-29 peak in the spectrum of 2-butanamine (**Figure 2.19**).

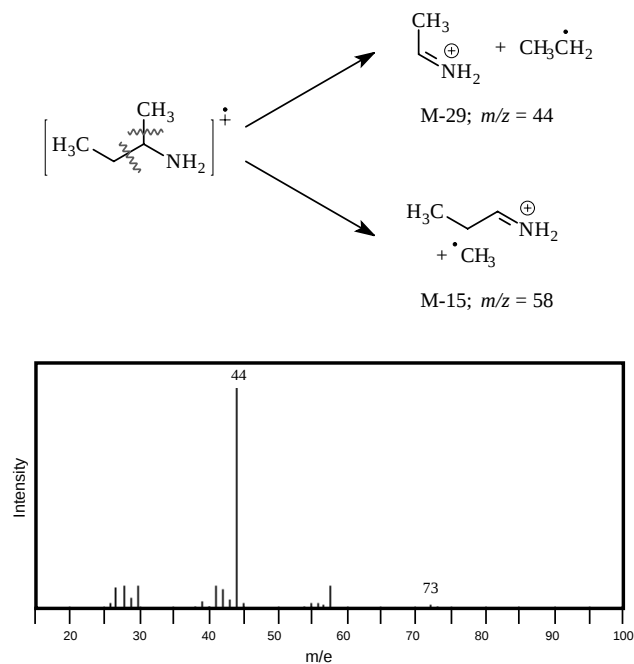


Figure 2.19 Mass spectrum of 2-butanamine.

Secondary and tertiary amines undergo similar cleavage, as shown by the M-15 peaks in the spectra for diethylamine and triethylamine (**Figures 2.20 and 2.21**).

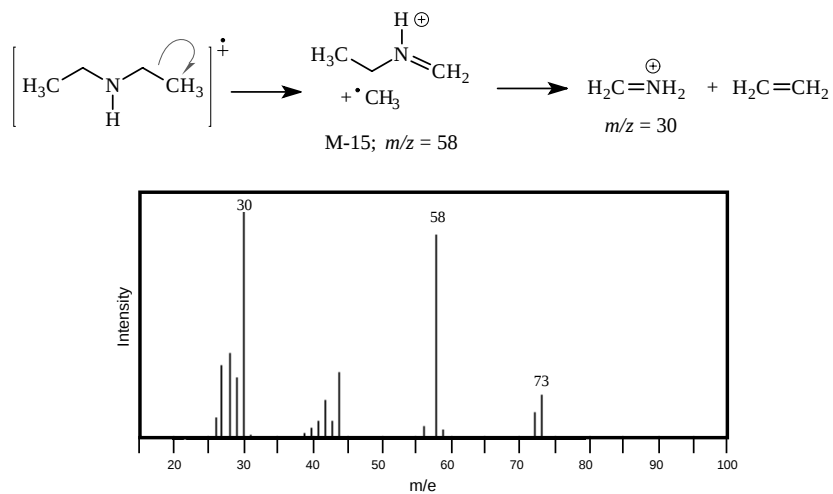


Figure 2.20 Mass spectrum of diethylamine.

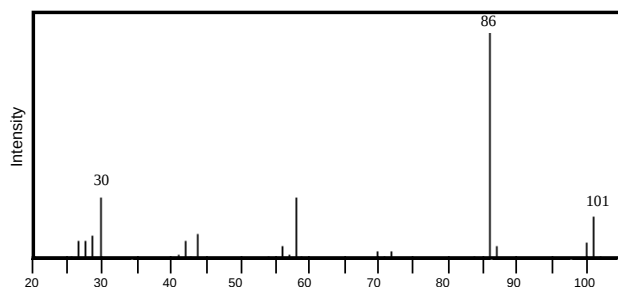


Figure 2.21 Mass spectrum of triethylamine.

Aromatic amines typically show intense molecular ions, a minor peak for M-1, and then further fragmentation due to loss of HCN (i.e., aniline, **Figure 2.22**).

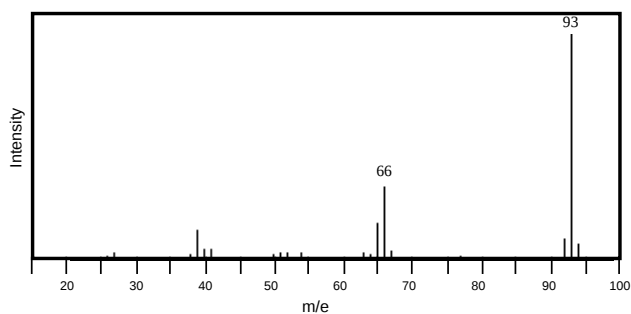
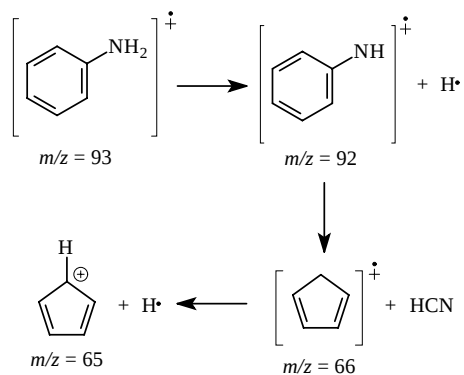
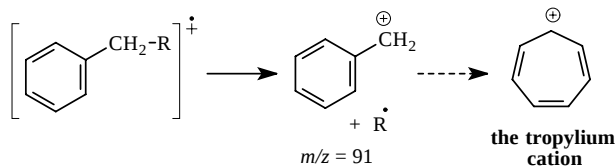


Figure 2.22 Mass spectrum of aniline.

Aromatic Hydrocarbons

The mass spectrum of benzene shows a strong molecular ion, which is the base peak, and little additional fragmentation is evident. This is because the fragmentation of a benzene ring is a high-energy process and simple pathways for the formation of stable ions do not exist. When an alkyl group is attached to a benzene ring, the preferred site of cleavage is at the benzyl carbon to give a peak at $m/z = 91$. This peak corresponds to C_7H_7^+ , the benzyl cation, or its rearrangement product, the **tropylium cation**. The tropylium cation is exceptionally stable because it is aromatic and the positive charge is delocalized over all seven ring carbons.



The mass spectrum of propyl benzene is shown in **Figure 2.23**. A decent molecular ion is evident at $m/z = 120$, with the major cleavage being loss of an ethyl radical ($M - 29$) to give the benzyl (or tropylium) cation at $m/z = 91$.

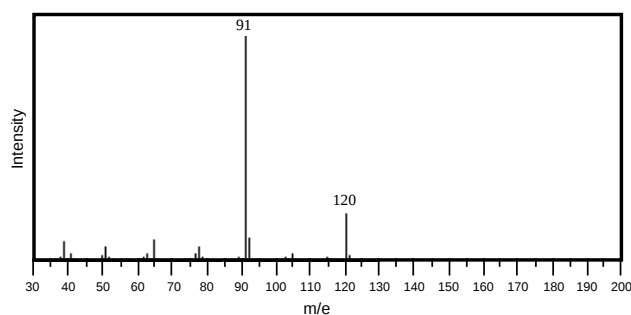


Figure 2.23 Mass spectrum of propyl benzene.

When an aryl hydrocarbon is branched at the benzyl position, cleavage and rearrangement occurs to generate a substituted tropylium ion. This is evident in the mass spectrum of isopropyl benzene (cumene, **Figure 2.24**).

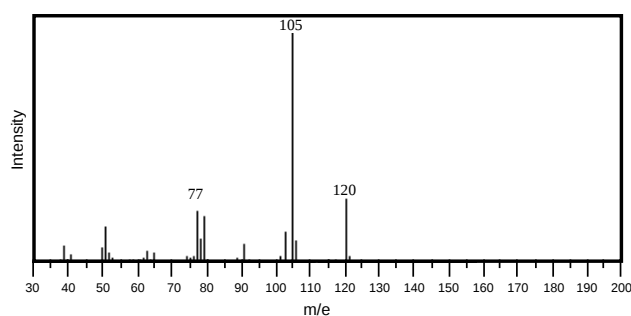
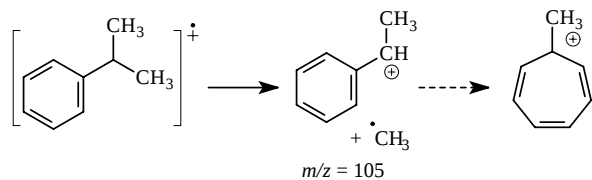


Figure 2.24 Mass spectrum of isopropylbenzene (cumene).

Carboxylate Esters and Carboxylic Acids

The most important cleavage reaction of carboxylate esters is loss of the alkoxy group to form the oxocarbenium ion. In the mass spectrum of methyl propanoate (**Figure 2.25**), the molecular ion at $m/z = 88$ fragments with loss of a methoxy radical to give the oxocarbenium ion at $m/z = 57$, which can expel CO to give the ethyl carbocation at $m/z = 29$. In this spectrum, the peak from the cleavage on the opposite side of the carbonyl is also evident; the fragment $\text{CH}_3\text{--O--CO}^+$ at $m/z = 59$.

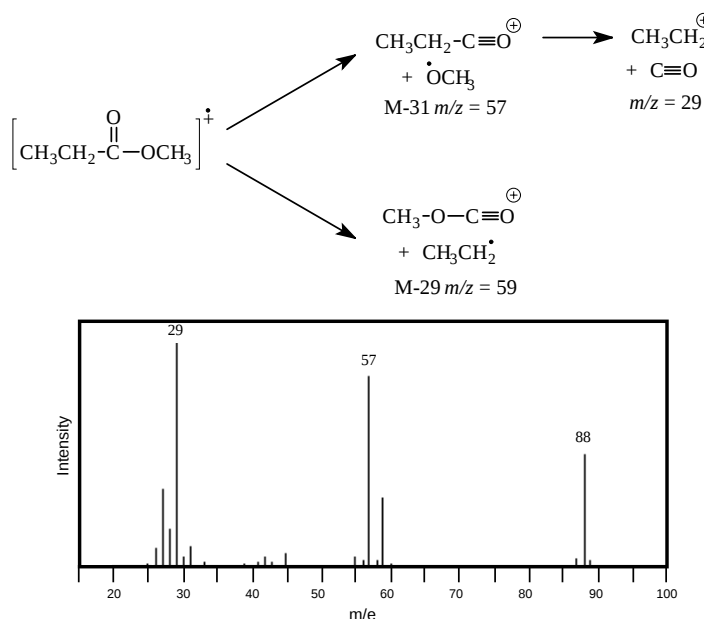
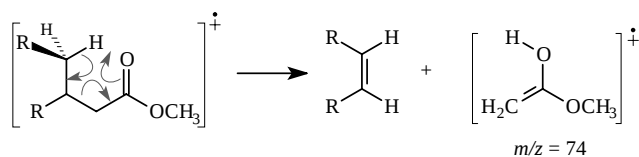


Figure 2.25 Mass spectrum of methyl propanoate.

Methyl esters with alkyl side-chains readily undergo McLafferty rearrangement reactions producing cation radicals with $m/z = 74$.



Benzyl esters undergo rearrangement to eliminate neutral ketene and form the benzyl alcohol cation radical (i.e., benzyl acetate, **Figure 2.26**). The fragmentation of benzyl alcohols to form the even-electron benzyl cation (with expulsion of hydroxyl radical) is not a favorable process, in spite of the stability of the benzyl cation, and only a secondary peak is observed at $m/z = 91$ in this spectrum.

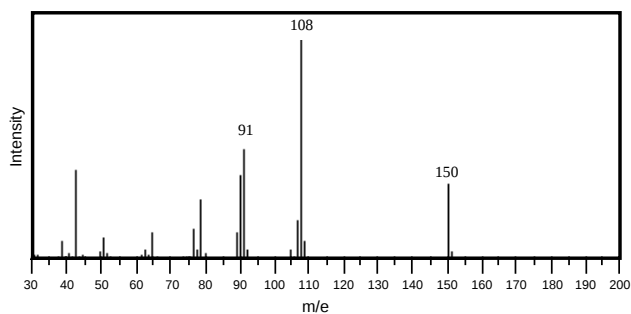
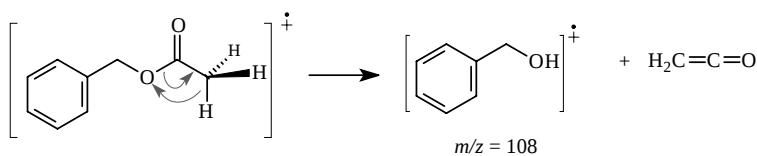


Figure 2.26 Mass spectrum of benzyl acetate.

The fragmentation in carboxylic acids is similar to that observed in simple esters, with α -cleavage being predominant and McLafferty rearrangements being observed with longer side-chains. The mass spectrum of benzoic acid (**Figure 2.27**) shows a strong molecular ion, a peak at $m/z = 105$, due to loss of the hydroxyl radical, and loss of CO to give the phenyl cation at $m/z = 77$.

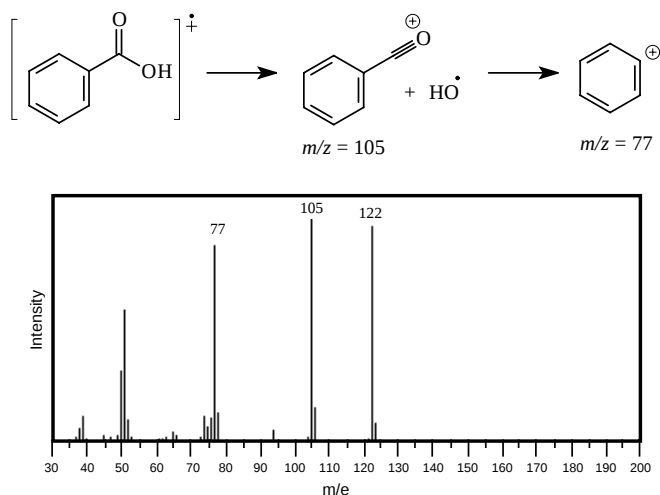


Figure 2.27 Mass spectrum of benzoic acid.

Ethers

Simple ethers cleave alpha to the carbon adjacent to the oxygen to give oxocarbenium ions. In ethyl methyl ether (**Figure 2.28**), loss of a methyl radical gives the base peak at $m/z = 45$.

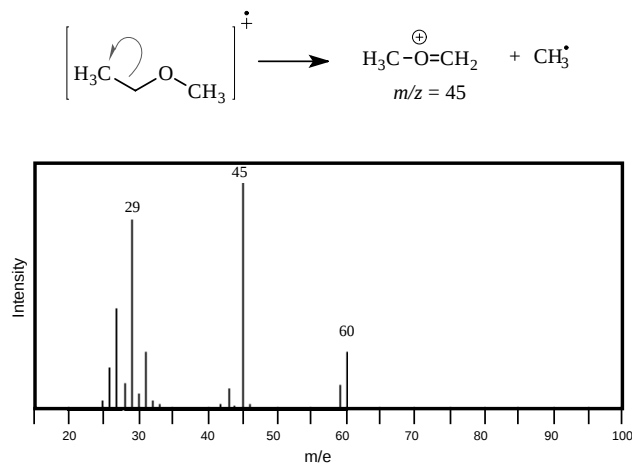


Figure 2.28 Mass spectrum of ethyl methyl ether.

Aromatic ethers (phenyl methyl ether; anisole, **Figure 2.29**) can fragment to lose the alkyl group, giving the $\text{C}_6\text{H}_5\text{O}^+$ ion ($m/z = 93$). Additionally, the alkoxy group can be lost to give C_6H_6^+ and C_6H_5^+ ions ($m/z = 78$ and 77).

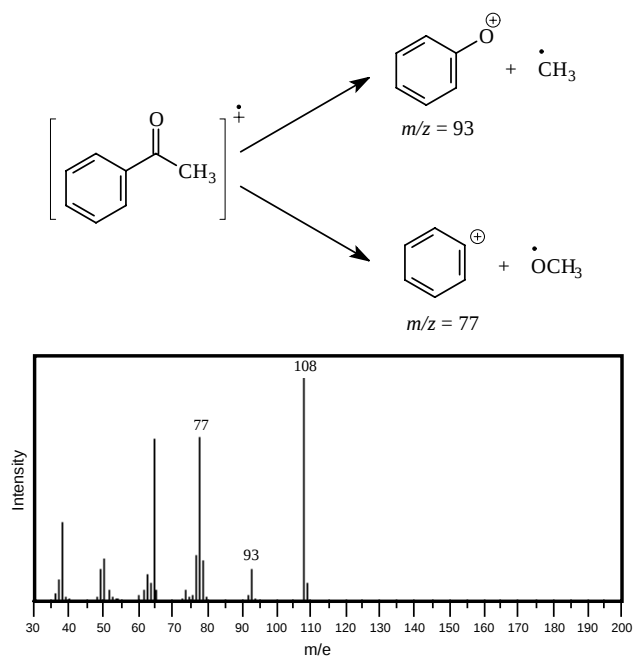


Figure 2.29 Mass spectrum of anisole.

Nitriles and Amides

Simple aliphatic nitriles display weak molecular ions in the mass spectrum and often show M-1 peaks due to the formation of ions of the type $\text{R}-\text{CH}=\text{C}=\text{N}^+$. For longer alkyl chains, McLafferty rearrangements are important, as shown below for butanenitrile (**Figure 2.30**, the molecular ion at $m/z = 69$ is not seen in this spectrum).

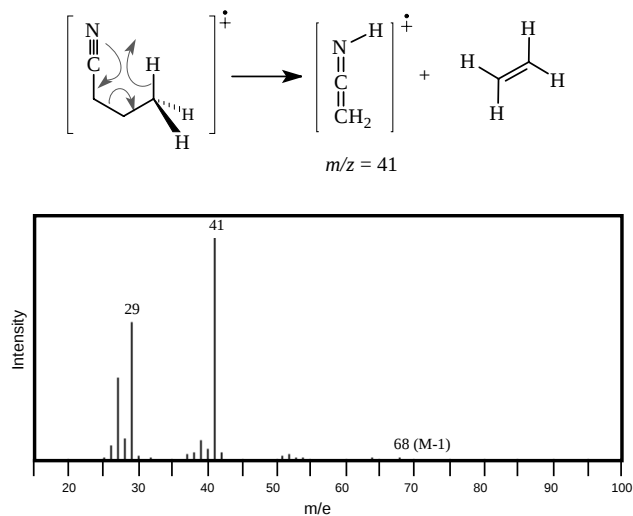


Figure 2.30 Mass spectrum of butanenitrile.

Aromatic nitriles show strong molecular ions (benzonitrile, **Figure 2.31**) and peaks for the loss of cyanide and the elements of HCN ($m/z = 77$ and 76 , respectively).

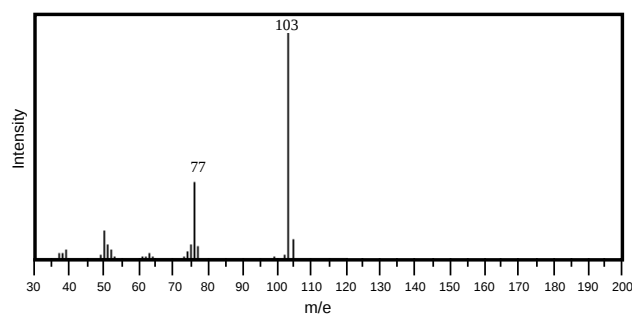


Figure 2.31 Mass spectrum of benzonitrile.

The mass spectrum of simple primary amides typically shows a moderate molecular ion and an intense peak at $m/z = 44$ due to loss of an alkyl radical (propanamide, **Figure 2.32**).

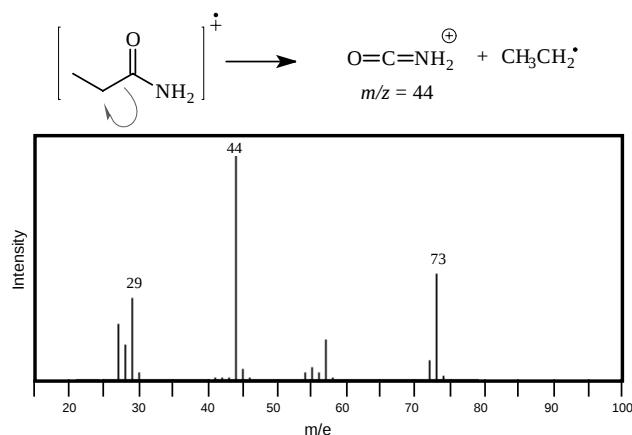
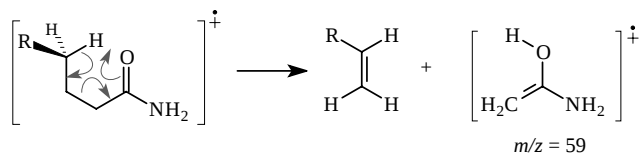


Figure 2.32 Mass spectrum of propanamide.

Long-chain amides, like esters, undergo McLafferty rearrangements. For primary amides, this generates a peak at $m/z = 59$.

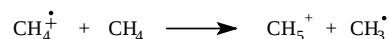


Other Techniques for Ionization

As described in the preceding sections, molecular ions formed in an **electron impact** mass spectrometer are high-energy species, and for many compounds, the molecular ions readily fragment and do not appear in the mass spectrum. Two other specialized methods have been developed to allow unstable molecular ions to be observed and studied more easily: **field ionization** and **chemical ionization**.

Field ionization utilizes a strong electric field, in the range of $10^7 - 10^8$ V/cm to ionize gas-phase samples. Rather than an electron beam, ionization occurs at the anode, which may be a sharp tip or very thin wire. Sample molecules in the vicinity of this wire undergo ionization to form molecular ions with low vibrational energies. These molecular ions lack the required activation energy for most fragmentation processes, hence the molecular ion in a field ionization mass spectrum is typically intense, with little or no fragmentation occurring. If the sample molecule is nonvolatile, solid sample can be applied directly to the anode (the fine tip) and gas-phase ions are formed as the positive molecular ions are repelled by the anode and *thrown* into the gas phase.

Chemical ionization utilizes proton transfer from strong Lewis acids to form molecular ions which are one mass unit *above* the molecular weight of the sample. In the chemical ionization mass spectrometer, the gas-phase sample is introduced at very low concentrations, along with a much higher concentration of a carrier gas such as methane. Methane undergoes electron impact ionization to form cation radicals in the usual manner, but because of the (relatively) high pressure of the gas, **bimolecular collisions** occur to produce species such as CH_5^+ .



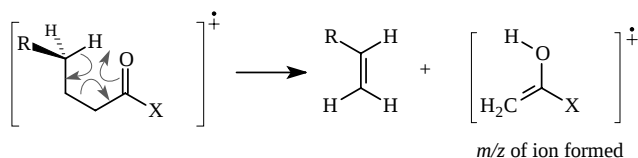
The CH_5^+ ion is a powerful Lewis (and Brønsted) acid and will react with neutral sample molecules to form protonated, gas-phase ions. These $M + 1$ ions do not have sufficient energy to undergo fragmentation (or only undergo low-energy fragmentations), and the resulting ions can be measured using the standard electron impact magnetic analyzer.

Summary of Useful Information

Relative intensities of molecular ions for compounds containing combinations of bromine and chlorine.

Relative Intensity				
Halogen	M	M + 2	M + 4	M + 6
Br	1.0	.98		
Br ₂	1.0	1.95	.95	
Br ₃	1.0	2.93	2.86	0.93
Cl	1.0	0.33		
Cl ₂	1.0	0.65	0.1	
Cl ₃	1.0	0.98	0.32	0.03
BrCl	1.0	1.30	0.32	
Br ₂ Cl	1.0	2.28	1.59	0.32
BrCl ₂	1.0	1.63	0.74	.010

Mass-to-charge ratios of mclafferty rearrangement ions for common carbonyl compounds.



Functional Group	X	m/z
Aldehyde	-H	44
Methyl Ketone	-CH ₃	58
Amide	-NH ₂	59
Carboxylic Acid	-OH	60
Ethyl Ketone	-CH ₂ CH ₃	72
Methyl Ester	-OCH ₃	74
Ethyl Ester	-OCH ₂ CH ₃	88

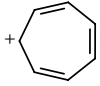
Primary fragmentations associated with some common functional groups.

Functional Group	Fragmentation
Amine	$\left[\begin{array}{c} \text{R}_1(\text{CH}_2)_n\text{N}-\text{CH}_2\text{R}_3 \\ \\ \text{R}_2 \end{array} \right]^+ \longrightarrow \text{R}_1(\text{CH}_2)_n\overset{\oplus}{\underset{ }{\text{N}}}=\text{CH}_2 + \text{R}_3^\bullet \longrightarrow \overset{\oplus}{\underset{ }{\text{HN}}}=\text{CH}_2 + \text{alkene}$
Aldehydes ($\text{R}_2 = \text{H}$) and Ketones	$\left[\begin{array}{c} \text{O} \\ \\ \text{R}_1-\text{C}-\text{R}_2 \end{array} \right]^+ \longrightarrow \text{R}-\text{C}\equiv\text{O}^\oplus + \text{R}_2^\bullet \longrightarrow \text{R}_1^\oplus + \text{CO}$
Halides	$[\text{R}-\text{X}]^+ \longrightarrow \text{R}^\oplus + \text{X}^\bullet$
Acyl Compounds	$\left[\begin{array}{c} \text{O} \\ \\ \text{R}_1-\text{C}-\text{X} \end{array} \right]^+ \longrightarrow \text{R}-\text{C}\equiv\text{O}^\oplus + \text{X}^\bullet$
Alcohols and Thiols	$\left[\begin{array}{c} \text{R}_1\text{CH}_2-\text{XH} \\ \\ \text{R}_2 \end{array} \right]^+ \longrightarrow \text{R}_1\text{CH}_2=\overset{\oplus}{\text{XH}} + \text{R}_2^\bullet$

Fragments commonly lost from molecular ions.

Mass	Group	Mass	Group
15	CH_3	32	CH_3OH
16	NH_2	44	C_3H_5
17	OH	42	CH_2CO
18	H_2O	42	C_3H_6
19	F	43	C_3H_7
20	HF	43	CH_3CO
26	C_2H_2	44	CO_2
29	CHO	44	C_3H_8
29	CH_2CH_3	45	CO_2H
30	CH_2O	45	OCH_2CH_3
31	OCH_3	46	$\text{CH}_3\text{CH}_2\text{OH}$

Masses and possible structures of common fragment ions.

<i>m/z</i>	Associated Structures
29	CHO^+ , CH_3CH_2^+
30	$\text{H}_2\text{C}=\text{NH}_2^+$
31	$\text{H}_2\text{C}=\text{OH}^+$
41	$\text{H}_2\text{C}=\text{CH}-\text{CH}_2^+$
42	$\text{H}_2\text{C}=\text{CH}-\text{CH}_3^+$
43	$\text{CH}_3\text{C}\equiv\text{O}^+$, $\text{CH}_3^+\text{CHCH}_3$
44	$\text{CH}_3\text{CHNH}_2^+$, CO_2^+ , $\text{O}=\text{C}=\text{NH}_2^+$, C_3H_8^+ , $\text{H}_2\text{C}=\text{CHOH}^+$
45	$\text{H}_2\text{C}=\text{OCH}_3^+$, $\text{CH}_3\text{CH}=\text{OH}^+$, CO_2H^+
54	$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2^+$
57	C_4H_9^+ , $\text{CH}_3\text{CH}_2\text{C}\equiv\text{O}^+$
58	$\text{CH}_3\text{CH}_2\text{NH}=\text{CH}_2^+$, $\text{H}_2\text{C}=\text{C}(\text{OH})\text{CH}_3^+$, $\text{CH}_3\text{CH}_2\text{CH}=\text{NH}_2^+$
59	$\text{CH}_3\text{CH}_2\text{CH}=\text{OH}^+$, $\text{H}_2\text{C}=\text{C}(\text{OH})\text{NH}_2^+$, $\text{H}_2\text{C}=\text{O}^+-\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{O}-\text{C}\equiv\text{O}^+$
60	$\text{H}_2\text{C}=\text{C}(\text{OH})\text{OH}^+$
65	C_5H_5^+ , $\text{H}-$ 
66	
67	
71	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{O}^+$ (and isomers)
72	$\text{H}_2\text{C}=\text{C}(\text{OH})\text{CH}_2\text{CH}_3^+$
73	$^+\text{O}\equiv\text{C}-\text{OCH}_2\text{CH}_3$
74	$\text{H}_2\text{C}=\text{C}(\text{OH})\text{OCH}_3^+$
76	C_6H_4^+
77	
78	C_6H_6^+
79 & 81	Br^+
80 & 82	HBr^+
85	$\text{C}_4\text{H}_9\text{C}\equiv\text{O}^+$
88	$\text{H}_2\text{C}=\text{C}(\text{OH})\text{OCH}_2\text{CH}_3^+$
91	 (and isomers)
105	$^+\text{O}\equiv\text{C}-$  , CH_3-  (and isomers)

Chapter 3

INFRARED SPECTROSCOPY

For organic molecules, molecular vibrations have energies that correspond to that of the infrared region of the electromagnetic spectrum. These molecular vibrations are typically measured using **infrared spectroscopy**. Within organic chemistry, the most useful range of the infrared spectrum encompasses approximately 2.5 to 15 μm (for example, the spectrum of isopropylbenzene, **Figure 3.1**). Positions of absorption bands in this spectrum are measured using wavelength (μm) or, more commonly, the reciprocal of the wavelength, cm^{-1} . The range of 2.5 to 15 μm corresponds to 4000 to 667 cm^{-1} ($1.0 \mu\text{m} = 1 \times 10^{-4} \text{ cm}$) and the reciprocal wavelength scale will be utilized throughout this book.

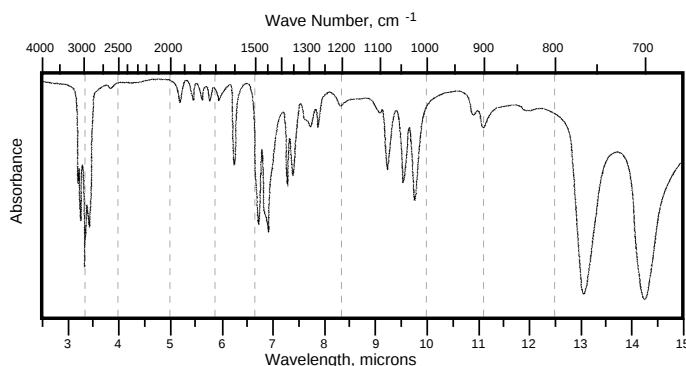


Figure 3.1 Infrared spectrum of isopropylbenzene (cumene).

Functional groups within organic chemistry have characteristic vibrational frequencies, and the presence of an absorption band in the infrared spectrum is strong suggestive evidence that the molecule contains that functional group. Likewise, for many “reliable” bands, the *absence* of an absorbance is also strong suggestive evidence that a particular functional group is absent, and both the presence and absence of characteristic bands will be utilized in this book in the characterization of unknown compounds.

Obtaining Infrared Spectra

Infrared spectra can be obtained on thin films of liquid samples, on samples in solution, on samples in the gas-phase, and on solid samples dispersed in an inorganic salt (typically KBr) or dispersed in a liquid hydrocarbon (a Nujol mull). With liquid samples, a reference cell is generally utilized to allow the solvent bands to be automatically subtracted by the spectrophotometer. Solid samples in KBr (when it is dry) generally do not have interfering bands, while Nujol mulls will have the spectral bands of the hydrocarbon superimposed on the spectrum of the sample.

Two types of infrared spectrometers (or spectrophotometers) are in common use; the classic **dispersive** instrument, and the computerized **Fourier transform** spectrometers. In the simple dispersive instrument, infrared radiation from a source (often called a *glow-bar*) is passed through the sample, focused on a monochromator, and then is *dispersed* into a continuous spectrum of infrared light. A slit allows a narrow wavelength band to fall on the detector circuitry, that produces a voltage in response to the intensity of the radiation. This voltage is compared with a *reference* voltage, where the infrared radiation has been passed through a reference sample (or simply the atmosphere) and difference in the intensity of the radiation passing through the sample and reference beams is expressed as the **percent transmittance (%T)**,

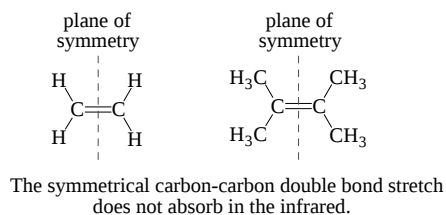
$$\text{percent transmittance} = \frac{I_s}{I_r} \times 100$$

where I_s is the intensity of the sample beam and I_r is the intensity of the reference beam. The transmittance of light through the sample is often expressed as the **absorbance**, which is negative logarithm of the ratio of the intensities, such that 100 %T is equal to an absorbance of zero. When radiation at a given wavelength is selectively absorbed by the sample, the sample is said to have a **peak** at that wavelength.

In a Fourier transform spectrometer, the optical path is designed to produce an interference pattern, called an **interferogram**. The interferogram is a complex wave-form that contains information from all of the frequencies in the infrared spectral region. A mathematical operation, termed a **Fourier transform** is utilized to deconvolute the interferogram and produce a frequency-domain spectrum that is identical to that obtained in the classical dispersive instrument. The advantage of Fourier transform infrared (FT-IR) is that an entire spectrum is obtained within a few thousandths of a second. Therefore, hundreds of complete spectra can be rapidly obtained on a sample, stored in computer memory, and the Fourier transform performed on the accumulated interferogram, achieving better signal-to-noise ratios than are generally available with dispersive instruments.

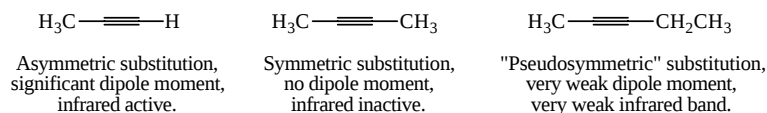
Symmetry Considerations in Infrared Spectroscopy

The absorbance of infrared radiation by a molecule serves to increase the amplitude of the specific molecular vibration that exactly matches the frequency of the absorbed radiation. Thus, an sp^3 carbon-hydrogen bond with an *average* stretching frequency of 3032 cm^{-1} will absorb that wavelength of infrared radiation and will display a band in the IR spectrum at 3032 cm^{-1} ($3.3\text{ }\mu\text{m}$). This simple correlation is true for all chemical bonds that possess a **dipole moment** that changes as a function of time. Generally, this requires that the bond X-X be unsymmetrical; symmetrical bonds, such as N_2 , do not absorb infrared radiation and are not seen in the infrared spectrum. The concept of symmetry extends beyond that of simple diatomic molecules to include molecules containing planes of symmetry. Thus, the carbon-carbon double bonds in ethene or in 2,3-dimethyl-2-butene do not absorb in the infrared.



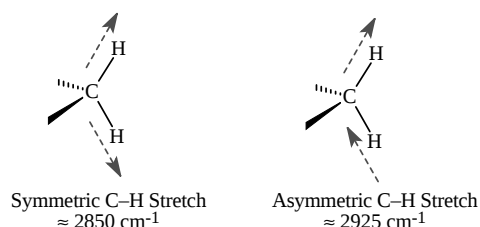
In practice, this restriction extends beyond true symmetry and molecules that are **pseudosymmetric** (having groups that are *similar*) generally show weak absorptions in the infrared.

Conversely, the more asymmetric a given bond is, and the larger the local dipole moment, the more intense the infrared absorption will be.



The simplest vibrational modes associated with the infrared spectrum are **stretching** and **bending**. Other, more complex modes also exist (**rocking**, **wagging**, **twisting**, and **scissoring**), but these absorbance bands often overlap and are not clearly associated with unique functional groups, making them less useful to the organic chemist.

For functional groups containing two or more identical atoms (i.e., $-\text{CH}_3$, $-\text{CH}_2-$, $-\text{NO}_2$, $-\text{NH}_2$, and carboxylic acid anhydrides), there are two distinct stretching modes; **symmetric** and **asymmetric**. Using the methylene group as an example, symmetric stretching involves **simultaneous** movement of the two hydrogens away from (and then toward) the central carbon atom; the typical symmetric CH stretch in a methylene group occurs at about 2850 cm^{-1} . Asymmetric stretching involves coupled, but **opposite** movement of the hydrogens toward and away from the central carbon, and occurs at about 2925 cm^{-1} .



For simple asymmetric bonds, the stretching frequency parallels the bond strength. Carbon-carbon triple bonds stretch at about 2150 cm^{-1} , carbon-carbon double bonds at about 1650 cm^{-1} and carbon-carbon single bonds at about 1200 cm^{-1} . Likewise, carbon oxygen double bonds in carbonyl groups stretch at about 1720 cm^{-1} while the carbon-oxygen single bond stretches at about 1100 cm^{-1} . The relationship between bond energy for two atoms of masses m_1 and m_2 and the force constant for a given bond, K , can be described by **Hooke's Law**, defined as:

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \quad \text{where,}$$

$\bar{\nu}$ = frequency in cm^{-1}

c = velocity of light, $3 \times 10^{10} \text{ cm/sec}$

K = force constant in dynes/cm

$\mu = \frac{m_1 m_2}{m_1 + m_2}$ the reduced mass

If the value of the force constant is known, this method can be utilized to estimate the stretching frequency with a fair degree of accuracy. Conversely, observed infrared stretching frequencies can also be utilized to calculate force constants.

Infrared Spectroscopy and the Organic Chemist

The infrared spectrum of a compound contains a great deal of information regarding the structure of the molecule. In practice, there is generally *too much* information available in the infrared spectrum, and interpreting a complete spectrum at high resolution is a mind-boggling (yet rewarding) exercise. If the purpose of obtaining an infrared spectrum is to help elucidate an unknown structure, the process of interpretation can be greatly simplified by focusing on those absorption bands that are simply and reliably associated with selected functional groups.

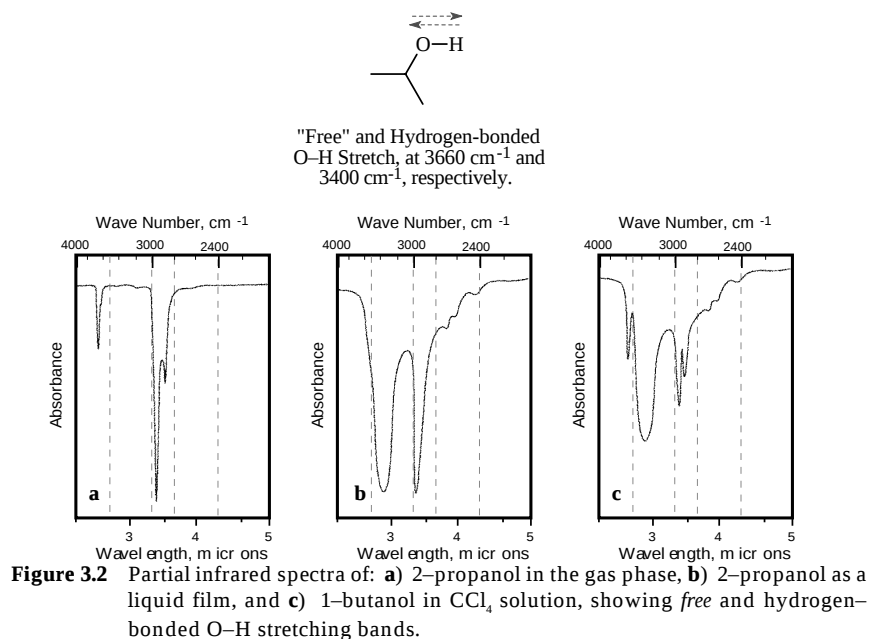
In general, this restricts close inspection of the infrared spectrum to the region $4000\text{--}1500\text{ cm}^{-1}$. The region of the spectrum below 1500 cm^{-1} contains stretching bands for carbon-carbon single bonds, along with bands associated with bending, wagging, rocking, etc. The complexity of this region makes it generally unsuitable for (rapid) interpretation, but the region as a whole is useful as it constitutes a **fingerprint** for a given molecule. The fingerprint region of the infrared spectrum is a useful method to establish the identity of an unknown molecule, relative to a known standard. You should be aware, however, that the details of this fingerprint are a function of sample preparation, spectrometer resolution and noise-reduction algorithms, that often compromise this utility.

In our discussion of *reliable* bands, we will begin at the high-energy of the spectrum (high wave numbers) and proceed down toward the fingerprint region. Several bands below 1500 cm^{-1} that are “often useful” will also be discussed, with the knowledge that many other absorbencies in this region can overlap and interfere with the interpretation.

The Interpretation of Infrared Spectra

Region #1: $3600\text{--}3300\text{ cm}^{-1}$, the O–H and N–H Stretch

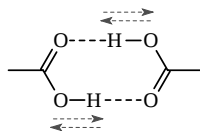
The O–H bond is asymmetric and absorbs infrared radiation in the region around 3400 cm^{-1} . The simple *free* O–H stretch is a high-energy band of medium intensity that occurs at about 3600 cm^{-1} . Generally the band is quite sharp, as seen in the gas-phase IR of 2-propanol. In this gas-phase spectrum, the O–H stretch occurs at 3660 cm^{-1} (**Figure 3.2a**).



The spectrum in this region contrasts sharply with the O–H band observed for 2-propanol, recorded as a liquid film (**Figure 3.2b**). The difference is due to **intermolecular hydrogen bonding**, that tends to weaken the force constant of the O–H bond, moving the absorbance to lower energy (lower wave number). Further, because hydrogen bonding in solution is dynamic, at any one instant there will be a distinct population of energies associated with hydrogen-bonded hydroxyl groups, each with its own characteristic absorption band. The result is that the average peak is shifted to lower energy, and is **highly broadened**. For alcohols in dilute solution (in a solvent like CCl_4) the O–H stretch is often resolved into *free* and *hydrogen-bonded* components, as seen in **Figure 3.2c**.

The hydroxyl group of phenols absorbs in this same region and is generally broader than that for simple alcohols, although this difference is difficult to exploit in practice.

The carboxylic acid O–H stretch is **extremely broad** and often spans the region from 3400 to 2400 cm^{-1} (**Figure 3.3**, 3-phenylpropanoic acid). This band arises from the strong hydrogen bonding present in the carboxylic acid dimer and is characteristic of carboxylic acids, although it often obscures much of the higher-energy region of the infrared spectrum.



Hydrogen bonding in carboxylic acids broadens the O–H stretch, often covering the region from 3400 to 2400 cm^{-1} .

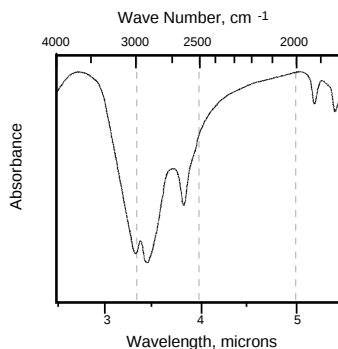
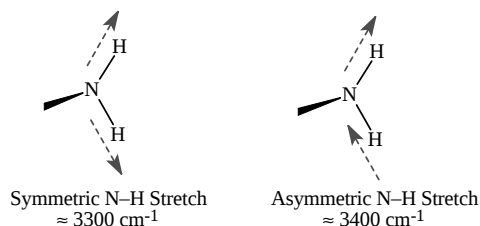


Figure 3.3 Partial infrared spectrum of 3-phenylpropanoic acid showing the broad, intense O–H band extending from 3400 to 2700 cm^{-1} .

Simple primary amines in the liquid phase typically display two medium-intensity, somewhat broadened absorbance bands in the range 3400 to 3300 cm^{-1} (benzylamine, **Figure 3.4a**). The two bands arise from symmetric and asymmetric stretching, and are generally sharper and somewhat less intense than absorbance bands from alcohols. The position of these bands can shift, slightly, on dilution in a solvent (CCl_4) and the bands are extremely weak in the gas-phase.



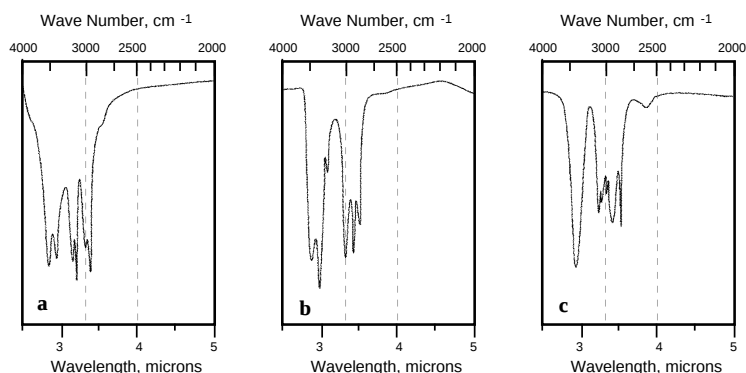


Figure 3.4 Partial infrared spectra of: **a)** benzylamine, **b)** 4-methylaniline, and **c)** N-methylaniline, showing the N-H stretching region.

Unsubstituted arylamines also display two bands in this region (4-methylaniline, **Figure 3.4b**), while N-methylaniline (**Figure 3.4c**) displays only a simple N-H stretch. Similar bands are observed in this region for primary (unsubstituted) and N-substituted amides. The O-H and N-H stretching vibrations are “highly reliable” bands in the infrared spectrum and should be noted for either their presence or absence; that is, for a compound containing oxygen, the *absence* of an O-H stretch is strong evidence that the compound is *not* an alcohol.

Region #2: 3300–3000 cm^{-1} , the sp and sp^2 C-H Stretch

The grid at 3000 cm^{-1} in the infrared spectrum is a convenient marker to separate *unsaturated* and *saturated* C-H stretching bands and generally hydrogens attached to sp and sp^2 carbons will display bands in the region *above* 3000 cm^{-1} . The C-H stretch for terminal alkynes is generally a sharp, intense band that occurs at about 3300 cm^{-1} (**Figure 3.5a**, 3-chloro-1-propyne). This band is typically stronger and higher (in wave number) than the bands associated with sp^2 C-H stretching, that can be weak and are often obscured in the spectrum. This is seen in the infrared spectrum in this region for cyclohexene, where the peak at 3100 cm^{-1} appears minor, relative to the absorbencies below 3000 cm^{-1} (**Figure 3.5b**). Aryl sp^2 C-H stretching occurs in this same region, as shown for ethylbenzene (**Figure 3.5c**) where the sp^2 C-H occurs at about 3050 cm^{-1} .

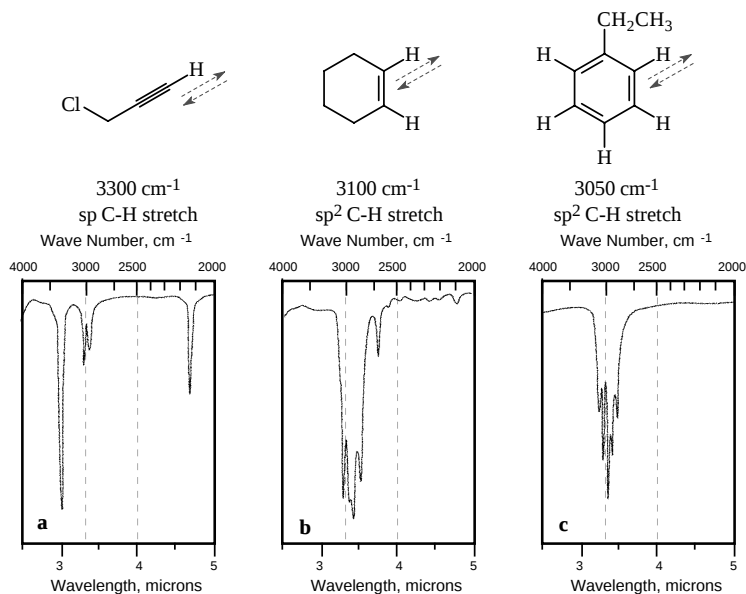


Figure 3.5 Partial infrared spectra of: **a)** 3-chloro-1-propyne, **b)** cyclohexene, and **c)** ethylbenzene, showing the sp and sp^2 C-H region.

The sp C–H stretching vibration of a terminal alkene is “highly reliable” and should be noted for either its presence or absence. Alkene and arene C–H stretching vibrations are not as reliable, both because of their weak-to-medium intensities and the fact that they are often obscured by more dominant bands in the region. In general, the presence of a clear band in this region can be taken as good evidence for sp^2 C–H, but quite often an honest interpretation of this region is that the evidence is “inconclusive” (or often restated as “I haven’t a clue!”).

Region #3: 3000–2900 cm^{-1} , the sp^3 C–H Stretch

The C–H bonds of methyl and methylene groups show symmetric and asymmetric stretching bands in the region immediately below 3000 cm^{-1} in the infrared spectrum. Classic examples of the sp^3 C–H stretch are the spectra for 1-bromo-2-methylpropane, methylcyclohexane, and cyclohexene (Figures 3.6, a, b & c).

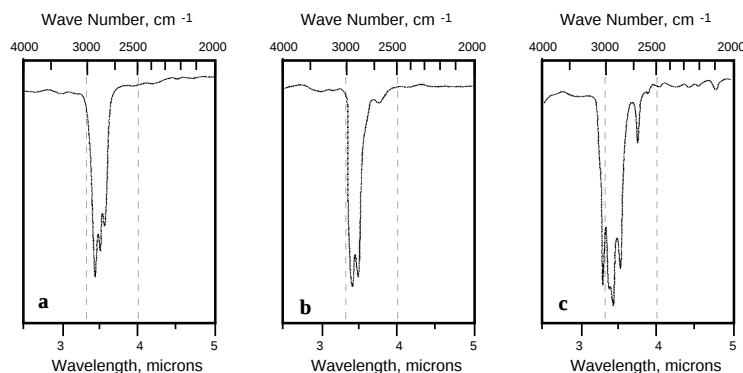


Figure 3.6 Partial infrared spectra of: **a)** 1-bromo-2-methylpropane, **b)** methylcyclohexane, and **c)** cyclohexene, showing the sp^3 C–H stretching region.

In the spectrum of cyclohexene, the separation between sp^2 C–H (3100 cm^{-1}) and sp^3 C–H (2900 cm^{-1}) is clearly apparent. As shown in these examples, the sp^3 C–H is typically medium-to-strong in intensity and is generally regarded as a “reliable” infrared band. Although it is *reliable*, it is not especially *useful*, because most simple organic molecules contain sp^3 C–H. The *absence* of this band is generally more informative than its presence.

Region #4: 2850–2750 cm^{-1} , the Aldehyde sp^2 C–H Stretch

The C–H stretch of aldehydes is a band that is often useful in distinguishing aldehydes and ketones. Aldehydes will generally display two bands in this region, with the lower one being the most important because it is generally well-separated from alkane C–H stretching bands. This is clearly seen in the partial spectrum of butanal (Figure 3.7) where the aldehyde CH stretching bands (2805 and 2705 cm^{-1}) are clearly separated from the sp^3 C–H bands (2968 and 2895 cm^{-1}).

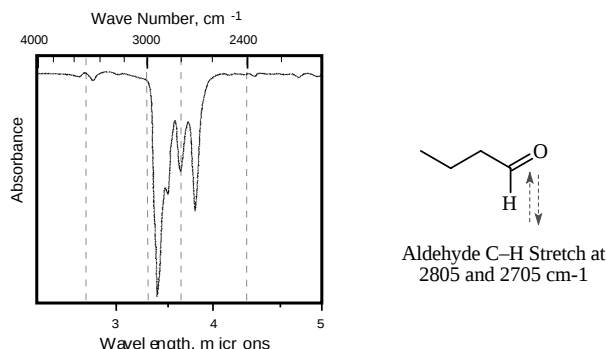


Figure 3.7 Partial infrared spectrum of butanal, showing the aldehyde C–H stretching region.

Although the aldehyde C–H stretch is typically weak, it occurs in a region of the spectrum where there is little interference (especially the lower band) and therefore qualifies as “somewhat reliable” and “often useful”.

Region #5: 2250–2150 cm^{-1} , the Nitrile $\text{C}\equiv\text{N}$ and Alkyne $\text{C}\equiv\text{C}$ Stretching Bands

As described in the introduction, in order for a bond to absorb infrared radiation, it must possess a dipole moment, and the more asymmetric that dipole, the more intense the band generally will be. The carbon–nitrogen triple bond of nitriles has a dipole of medium intensity, and the triple bond stretch of nitriles occurs as a medium-to-strong band in the region around 2250 cm^{-1} (**Figure 3.8a**, malononitrile).

Carbon–carbon triple bonds, however, generally lack a significant dipole moment and, with the exception of terminal alkynes, present only very weak bands in this region (**Figures 3.8b**, 2-chloro-1-butyne, and **3.8c**, 1-propynylbenzene).

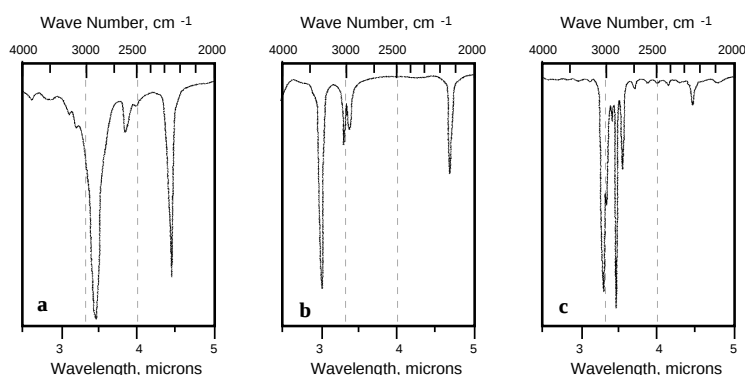


Figure 3.8 Partial infrared spectra of: **a**) malononitrile, **b**) 2-chloro-1-butyne, and **c**) 1-propynylbenzene, showing the $\text{C}\equiv\text{X}$ stretching region.

The *triple bond* region, 2250–2150 cm^{-1} , is generally uncluttered by other functional groups and the triple bond stretch for nitriles is typically significant, making this region of the spectrum useful for the identification of nitriles. Terminal alkynes often present a useful absorbance in the region, making it worth examining, but you should always remember that alkynes possessing symmetry or pseudo symmetry will not show any significant absorption.

Region #6: 1800–1650 cm^{-1} , the Carbonyl $\text{C}=\text{O}$ Stretch

The carbonyl $\text{C}=\text{O}$ stretch is one of the most useful absorbance bands in the infrared spectrum. The carbonyl $\text{C}=\text{O}$ bond poses a large dipole moment and the infrared spectrum of most carbonyl compounds is dominated by the absorbance of this functional group (for example, acetone, **Figure 3.9**).

The carbonyl stretch of aldehydes, ketones and simple acyl compounds occurs in the region between (about) 1800 and 1650 cm^{-1} . The exact position of the carbonyl absorbance within this region roughly parallels the reactivity of the carbonyl carbon in nucleophilic addition reactions; that is, the more reactive the carbonyl, the higher the observed absorbance band. While this correlation is far from exact, it does present an easy way to remember the relative positions of carbonyl carbons within this region. As shown in **Figure 3.10**, the highest frequency carbonyl stretches are observed in acid anhydrides and acid halides, that are both very reactive in simple acyl transfer reactions.

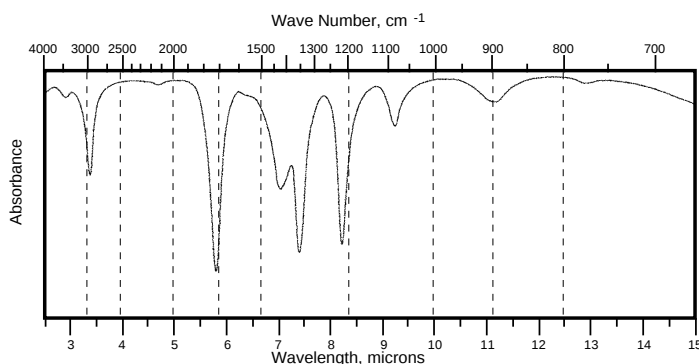


Figure 3.9 Infrared spectrum of 2-propanone (acetone); note the strong carbonyl absorbance.

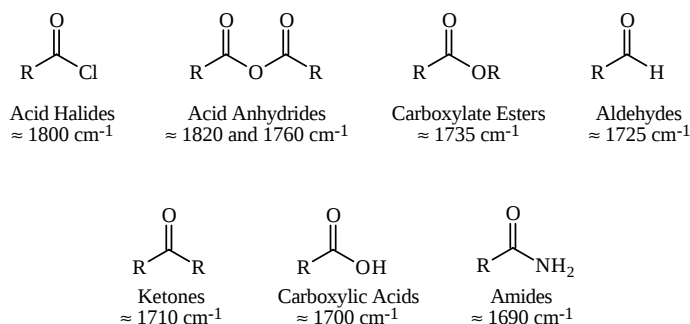


Figure 3.10 Approximate carbonyl stretching frequencies for common acyl derivatives.

Acid halides generally have a significant band at about 1800 cm^{-1} (**Figure 3.11a**, hexanoyl chloride; 1804 cm^{-1}) while acid anhydrides typically display two bands (asymmetric and symmetric stretching, respectively), as seen for hexanoic anhydride (**Figure 3.11b**; 1824 and 1759 cm^{-1}).

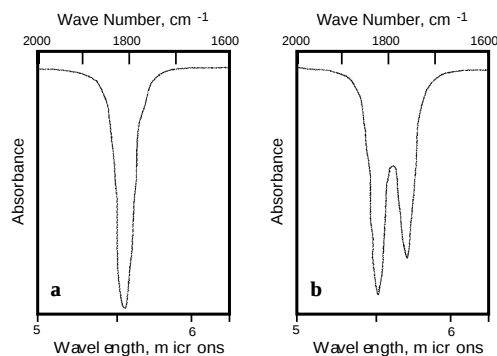


Figure 3.11 Partial infrared spectra of: **a)** hexanoyl chloride, and **b)** hexanoic anhydride, showing the carbonyl stretching region.

Carboxylic esters are observed in the region around 1735 cm^{-1} , while aldehydes and ketones generally appear at about 1725 and 1710 cm^{-1} , respectively. Carboxylic acids and amides are the *least reactive* carbonyls toward simple acyl transfer and their $\text{C}=\text{O}$ stretching bands are at the bottom of the carbonyl range, as shown for 2-phenylethanoic acid and *N*-methylacetamide (**Figure 3.12a**, 1700 cm^{-1} and **3.12b**, 1688 cm^{-1} , respectively).

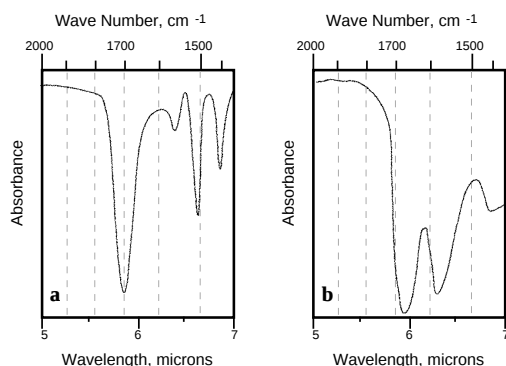


Figure 3.12 Partial infrared spectra of: **a)** 2-phenylacetic acid, and, **b)** *N*-methylacetamide, showing the carbonyl stretch region.

The spectrum of *N*-methylacetamide also shows the strong amide N–H bending vibration at 1590 cm^{-1} . This absorbance is sometimes called the *amide-II band* and is sometimes useful in studying the secondary structure of peptides and small proteins.

Conjugation of a carbonyl with an adjacent π -system tends to increase the single-bond character of the carbon–oxygen double bond, lowering the force constant for the stretching vibration, and consequently, lowering the frequency of the carbonyl absorption. For simple carbonyl compounds, this effect is roughly 25 cm^{-1} ; thus, the carbonyl absorbance for benzaldehyde (1700 cm^{-1}) is about 25 wave numbers **lower** than a simple saturated aldehyde (1725 cm^{-1}).

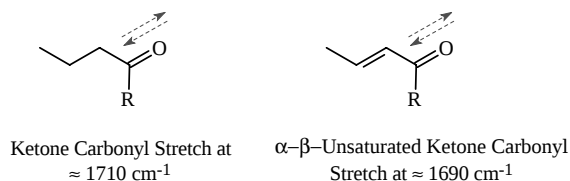


Figure 3.13 Effect of unsaturation on the carbonyl stretch frequency.

Ring strain has the opposite effect on the position of the carbonyl stretch. A strained cyclic ketone, such as cyclobutanone, will have a carbonyl stretch that is 60 to 70 wave numbers **higher** than a simple acyclic ketone (1780 , compared to 1710 cm^{-1}). This effect varies with ring size and carbonyl in larger rings (cyclohexanone, 1715 cm^{-1}) are typical of simple ketones. Again, the simple analogy can be followed; carbonyls in strained rings are more reactive toward nucleophilic substitution and are therefore found at higher frequencies.

Carbonyl stretching absorptions in the infrared are among the “most reliable” diagnostic peaks in the spectrum and should be noted for either their presence or absence. While the exact stretching frequency can be altered by conjugation, strain, etc., the *limits* of the carbonyl range offer reliable evidence for the presence of highly reactive (acid halides and anhydrides) or relatively unreactive acyl groups (acids and amides), and the position of the carbonyl band should also be noted in a standard interpretation.

Region #7: $1650\text{--}1450\text{ cm}^{-1}$, the Carbon–Carbon Double Bond Stretch

The stretching bands from carbon–carbon double bonds are typically weak and are often difficult to observe and interpret. Terminal alkenes (**Figure 3.14a**, 1-octene) are generally the most intense, while the absorbance from substituted alkenes is generally very weak (**Figure 3.14b**, 2-methyl-2-pentene). Further, overtones from alkene out-of-plane bending modes often appear in the region between 1800 and 1600 and these are often more intense than the carbon–carbon stretch (for example, the band at 1710 cm^{-1} in the spectrum of 2-methyl 2-pentene, **Figure 3.14b**).

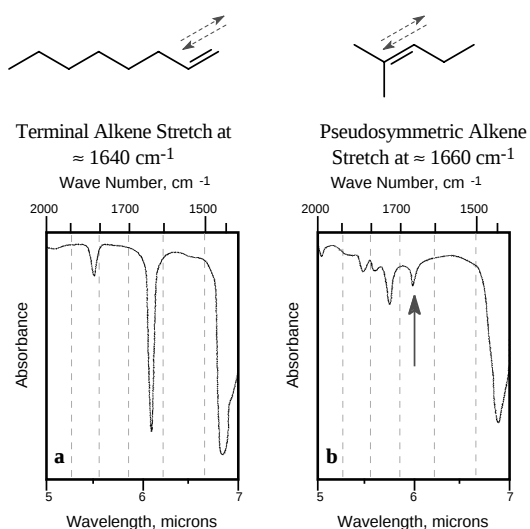


Figure 3.14 Partial infrared spectra of: **a)** 1-octene, **b)** 2-methyl-2-pentene, showing the carbon-carbon double bond stretching region.

The partial carbon-carbon double bond of arenes appears as a family of two to four sharp peaks in the region 1600 to 1450 cm^{-1} (**Figure 3.15**, polystyrene). These bands in a polystyrene film (1601 , 1583 , 1495 and 1454 cm^{-1}) are highly reproducible and are often utilized to calibrate simple dispersion spectrophotometers.

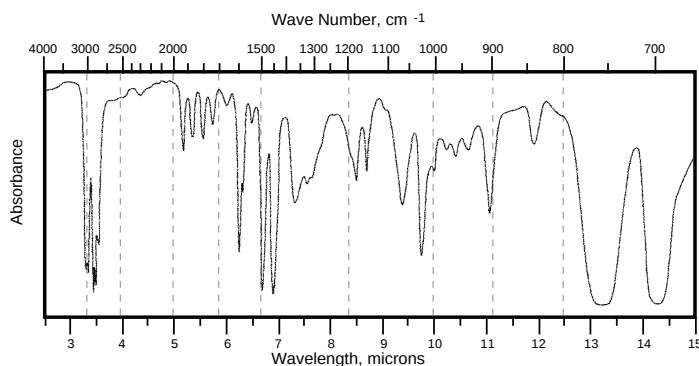


Figure 3.15. Infrared spectrum of a polystyrene film.

Most arenes will display two or more of these bands, in varying intensity, and with practice, the characteristic look of the group can be utilized reliably to suggest the presence of a benzene ring in an unknown. Because of the weak intensity of the carbon-carbon double bond stretch, the peak is relatively low priority, but can be diagnostic, especially for arenes.

Region #8: $1450\text{--}600\text{ cm}^{-1}$, the Fingerprint Region

As described previously, the region of the infrared spectrum below about 1500 cm^{-1} is generally complex for most organic molecules, and contains absorbance bands arising from bending, wagging, rocking, etc. Within this collection, there are a few bands that are worth remembering because they can often be useful in elucidating a structure. You should remember, however, that this region is complex and that the presence of a band at a given wavelength may be **consistent with** a structure, but should seldom be utilized as the basis for assigning functional groups to an unknown.

The **C–O stretch** occurs in this regions, typically between 1250 and 1000 cm^{-1} (**Figure 3.16**, 2-propanol). The absorbance is typically strong, and compounds containing a carbon-oxygen bond should display an intense band in this region. Again, the presence of this band is *consistent with* the assignment of a carbon-oxygen bond, but the presence of a band should not be utilized to *assign* a carbon-oxygen bond to your structure.

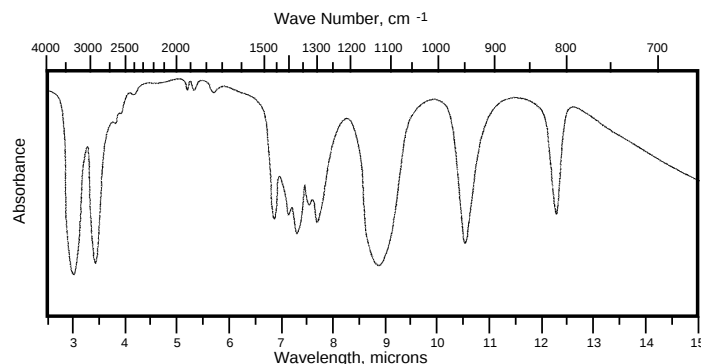


Figure 3.16 Infrared spectrum of 2-propanol; the C–O stretch is a strong band at 1120 cm^{-1} .

Out-of-plane bending modes on **disubstituted arenes** absorb in the region between 900 and 700 cm^{-1} . Again, these bands can often be utilized to *confirm* substitution patterns, but should not be the sole basis of an assignment. For simple arenes, typical patterns are summarized in **Table 3–1**. A nice example of these bands is seen in the spectrum of polystyrene on the preceeding page (**Figure 3.15**).

Table 3–1. Out-of-plane bending modes associated with substituted arenes.

Substitution	Compound	Absorbance Bands, cm^{-1}
Mono-substitution	Toluene	729, 695
Ortho di-substitution	1,2-Dimethylbenzene	740
Meta di-substitution	1,3-Dimethylbenzene	872 (weak), 766, 691
Para di-substitution	1,4-Dimethylbenzene	793

Carbon-hydrogen bending modes for simple alkyl groups occur in the region 1465 to 1350 cm^{-1} . For simple alkanes, these assignments are sometimes useful, but on more complex molecules it is difficult to rapidly obtain structural information. You are invited to refer to one of the many excellent textbooks that cover infrared spectroscopy in greater depth.

Chapter 4

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

One of the properties that quantum mechanics assigns to atomic nuclei is the property of **spin**, and the nuclear spin quantum number, I , is a function of the *atomic number* and the *atomic mass* of the nucleus. Nuclei that possess either an *odd mass* or an *odd atomic number* will have $I \neq 0$, and will have the property of *spin*. **Nuclear magnetic resonance (NMR)** is a spectroscopic method that allows examination of the properties of nuclei that have non-zero spin numbers. The technique is directly applicable to nuclei that are commonly present in organic molecules and is typically utilized within organic chemistry to examine the environment of protons (^1H) and the minor isotope of carbon, ^{13}C .

As seen in Table 4-1, the nuclear spin quantum number of these nuclei is $1/2$, that means that the nucleus possesses two *spin states*. As we will see, the interpretation of NMR spectra is greatly simplified by the fact that the common isotopes of carbon and oxygen (^{12}C and ^{16}O , 98% and 99.8% natural abundance, respectively) have $I = 0$, which means they lack the property of nuclear spin and are *NMR silent*.

Table 4-1. Spin quantum numbers and natural abundance of common nuclei.

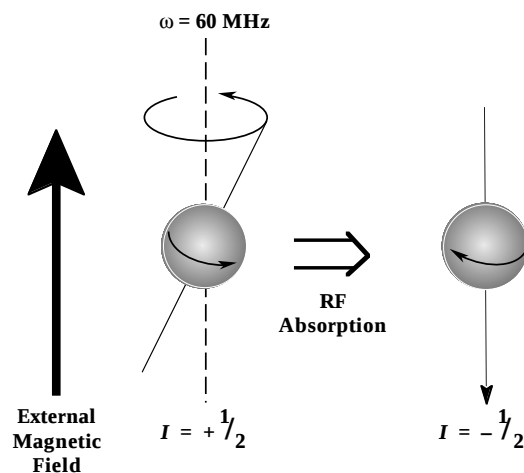
Nucleus	^1H	^2H	^{12}C	^{13}C	^{14}N	^{16}O	^{19}F	^{31}P	^{35}Cl
Quantum Number, I	$1/2$	1	0	$1/2$	1	0	$1/2$	$1/2$	$1/2$
Number of Spin States	2	3	0	2	3	0	2	2	4
% Natural Abundance	99.9	0.01	98	1.1	99.6	99.8	100	100	76

It is useful to think of nuclei with $I = 1/2$ as if they were physically spinning. Because the nucleus is charged, the process of *spinning* will generate a local electromagnetic field, consisting of electric and magnetic components. In the absence of an external magnetic field, the *orientation* of these local magnetic fields is random. If, however, a nucleus with the property of *spin* is placed in a magnetic field, the individual nuclear magnetic moments (μ) will assume one of two possible spin states: parallel to the applied field, or opposite to it ($+1/2$ or $-1/2$, respectively).

The energies of these two spin states are not equal, and the spin state of $+1/2$ (parallel to the applied field) is lower energy. The energy difference between the two spin states is a function of the applied magnetic field and the more powerful the magnetic field, the greater this energy difference. The *population density* of the two spin states is also not identical and there is a *very slight* excess of nuclei in the lower energy spin state. The population density of the spin states is also a function of the applied magnetic field, with the population of the low-energy state increasing as the strength of the applied field increases. In a simple NMR spectrometer with an external magnetic field of 1.41

Tesla, the population density in the lower energy spin state exceeds the high energy spin state by the factor 1,000,009 to 1,000,000; that is, the excess nuclei in the lower spin state is only 0.0009% of the total nuclei present. This excess increases with magnetic field strength, such that a powerful superconducting magnetic with a field strength of 14.1 Tesla will have an excess of about 0.0096%. This excess population is extremely important to consider since the signal the NMR spectrometer $^{1/2}$ detects arises *entirely* from the tiny percentage of excess nuclei in the lower spin state.

Although nuclei are described as aligning *parallel* or *anti-parallel* to an applied magnetic field, the axis of rotation of the nucleus is actually tilted away from the parallel by an angle, θ , where θ is a value that is greater than 0 and less than 90 degrees. Because the alignment is not truly parallel, the applied magnetic field imparts **spin angular momentum** to the nucleus, causing it to **precess** about its own axis of spin with a frequency, ω (the **Larmor frequency**). This precession generates an oscillating electric field of the same frequency. If electromagnetic radiation matching this frequency interacts with the precessing nucleus, the two electric fields can couple and energy from the radiation can be absorbed. When a nucleus absorbs energy in this manner, it undergoes a change in spin orientation (a *spin-flip*) and the nucleus is said to be in **resonance** with the incoming electromagnetic radiation.



If all nuclei of a given type underwent the change in spin orientation at the same frequency, NMR spectroscopy would be of little value. In fact, the frequency at which resonance occurs in a nucleus depends largely upon the electronic environment surrounding that nucleus. This is because the **valence electrons** around the nucleus are caused to *circulate* by the applied magnetic field. This circulation, termed a **local diamagnetic current**, induces a **local magnetic field** that is oriented to *oppose* the applied field. The net result is that the nucleus *feels* a reduced magnetic field; that is, the applied field has been **shielded** by the local diamagnetic current.

As a result of this shielding, the *effective* magnetic field on each nucleus in a molecule varies, depending on the local electron density. Since the frequency at which resonance occurs is a direct function of the effective magnetic field, every nucleus that is in a distinct electronic environment will undergo resonance at a different applied frequency. Thus, by varying the applied frequency, at a constant magnetic field (or the reverse, keeping the frequency constant and varying the magnetic field strength) each **magnetically equivalent** type of nucleus in a molecule can be individually induced into resonance, and detected.

The Pulsed Fourier Transform Spectrometer

In a continuous-wave spectrometer, nuclei are induced into resonance one equivalent group at a time by constantly varying the applied frequency or the field strength. In Fourier transform NMR, *all* of the nuclei of a molecule are excited at once by a very short **pulse** of radiation (lasting 1 to 10 μsec), covering a broad band of wavelengths. When the pulse is discontinued, the nuclei return to their previous spin states (or **relax**) and, in the process, each nucleus emits electromagnetic radiation. This emission, termed a **free-induction decay**, is amplified by the detector circuitry and typically stored in digital format in a host computer.

For a molecule containing only one type of resonance-active nuclei (i.e., the equivalent methyl groups of TMS) the free-induction decay will take the form of a sine wave of decaying amplitude, but with a fixed frequency (**Figure 4.2**). The frequency of this sine wave is a simple function of the frequency of the oscillator used to produce the *burst* and the frequency of the radiation emitted by the relaxing nucleus. Since the oscillator frequency is known, the frequency of the decay can be utilized to directly calculate the frequency (in Hz) of the nuclear resonance, which can be converted to the chemical shift of the nucleus in parts-per-million.

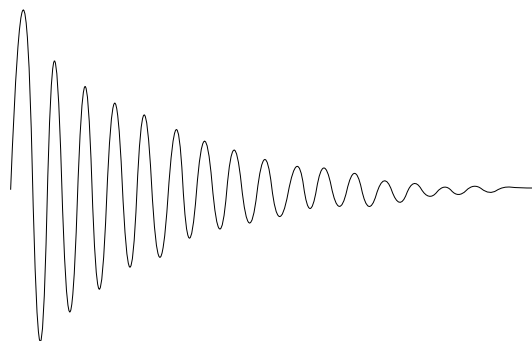


Figure 4.2 A time-domain free-induction-decay (FID) waveform for a single component.

Molecules that contain more than one type of resonance-active nuclei will produce a free-induction decay containing the frequencies for all of the nuclei in the molecule. In the FT-NMR, this free-induction decay waveform is saved on a host computer which deconvolutes the signal into individual frequencies for each nucleus using a mathematical method called a **Fourier transform**. The chemical shift for each type of nucleus (in ppm) is then plotted in standard format.

Because all nuclei in a molecule are excited at once in the FT-NMR, the complete spectrum can be acquired very rapidly. In general, the free-induction decay waveforms for many determinations are saved on the computer, and the analysis is performed on the accumulated signal. This signal averaging improves the signal-to-noise ratio in the final spectrum, and allows analysis to be performed on dilute samples that would not provide acceptable continuous-wave spectra.

Proton (^1H) NMR

Integration: Relative Signal Intensities

In the proton NMR, the *intensity* of the NMR signal is directly proportional to the number of equivalent hydrogens giving rise to that signal. In the ^1H NMR of dimethyl malonate (**Figure 4.3**) two peaks are evident with chemical shifts of 3.28 and 4.15 ppm. The intensity of the peaks is determined on the spectrometer by a procedure that is termed *integration*. In general, this is an electronic method that measures the area under a given NMR peak. These absolute areas are then expressed in terms of lowest whole-number ratios. In this text, these relative areas will be shown by small numbers associated with each peak. For dimethyl malonate, the ratio of the areas of the two peaks are 3 : 1, and the two peaks correspond to the six hydrogens of the equivalent methyl groups

(4.15 ppm) and the two equivalent hydrogens of the central methylene (3.28 ppm). In the problem sets in **Chapter 5**, these ratios are generally expressed in the ratios found in the unknowns (i.e., 6 : 2), to help guide interpretation.

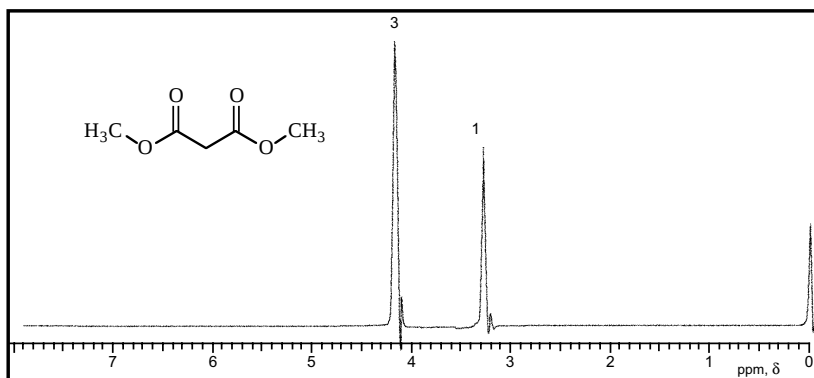


Figure 4.3 ^1H NMR of dimethyl malonate.

Chemical Shifts

The frequencies at which protons undergo resonance are a function of their electronic environment and can generally be related to neighboring functional groups. A simple correlation table showing common functional group effects is shown in **Figure 4.4**. These effects can be simply described as follows:

Simple sp^3 Hydrogens. Simple unstrained methyl and methylene hydrogens typically undergo resonance in the range **0.5 to 1.9 ppm**. Highly strained rings (cyclopropane) and simple methyl groups are at the low end of this range, while methylene and methyne hydrogens tend toward the high end.

Hydrogens adjacent to Mildly Electronegative Groups. The broad term *mildly electronegative* is used to include arenes, alkenes, alkynes, carbonyls, amines and sulfides. Hydrogens on carbons *adjacent* to these groups generally undergo resonance in the range **1.9 to 3.0 ppm**.

Hydrogens adjacent to Strongly Electronegative Groups. The broad term *strongly electronegative* is used to include halides, oxygen atoms and nitro groups. Hydrogens on carbons *adjacent* to these groups generally undergo resonance in the range **3.0 to 4.5 ppm**.

Alkene Hydrogens. Hydrogens attached *directly* to alkene sp^2 carbons typically undergo resonance in the range **4.5 to 6.9 ppm**.

Arene Hydrogens. Hydrogens attached *directly* to an arene (or an aromatic) ring undergo resonance in the range **7.0 to 8.0 ppm**.

Aldehyde Hydrogens. The hydrogen of the aldehyde group is highly deshielded, and typically undergoes resonance in the range **9.5 to 10.0 ppm**.

Carboxylic Acid Hydrogens. The hydrogen of the carboxylic acid group is the most highly deshielded hydrogen commonly encountered in organic chemistry, and typically undergoes resonance in the range **10.5 to 12.0 ppm**.

Exchangable Hydrogens. Hydrogens on alcohols, phenols, amines and amides have highly variable chemical shifts that depend on concentration, temperature and the solvent utilized. In general, alcohols and amines appear in the lower half of the spectrum (1 to 5 ppm) while phenols and amides are somewhat higher (4 to 8 ppm). The simple assignment of these peaks is difficult and is often best done by difference, looking at the δ -overs

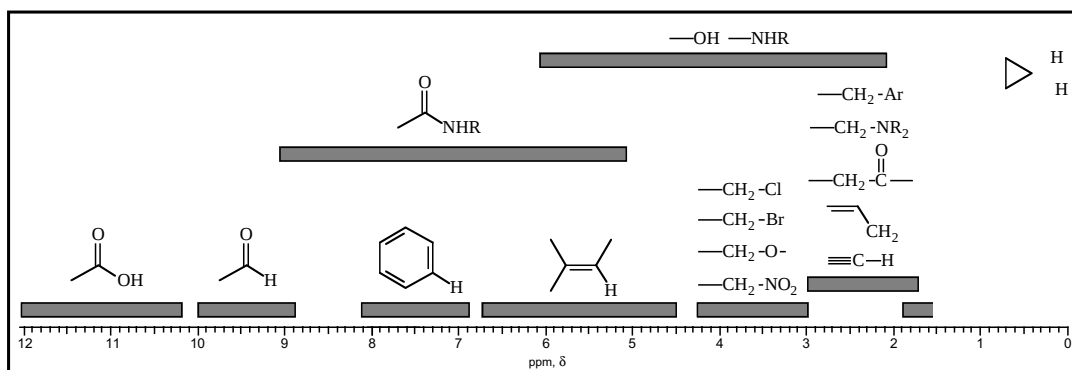


Figure 4.4 ^1H NMR chemical shifts of common functional groups.

Spin Coupling

Based on the considerations given above, the ^1H NMR spectrum of diethyl ether would be expected to consist of two peaks, one for the methyl group in the simple aliphatic region at about 0.95 ppm (integration of 3) and a second for the methylene group adjacent to the oxygen, with a chemical shift of about 3.75 ppm (integration of 2). The actual spectrum, shown in **Figure 4.5**, is much more complex than this. Although the predicted chemical shifts and integrations are observed, the spectrum consists of *seven* peaks, not two; the methyl group appears as a group of three peaks (a *triplet*) and the methylene as four peaks (a *quartet*).

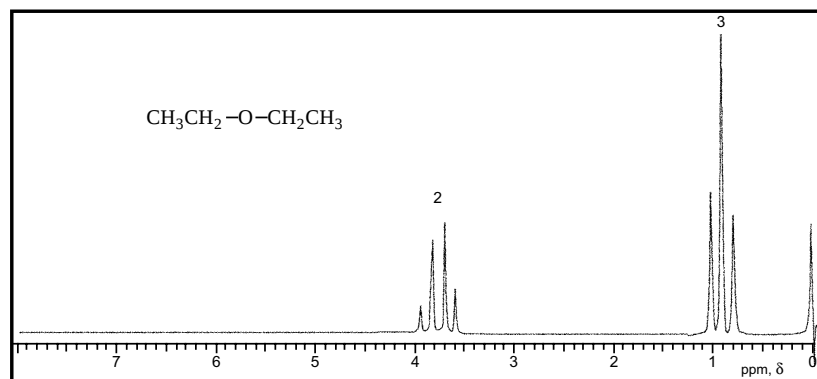


Figure 4.5 ^1H NMR of diethyl ether.

The multiplicity in this spectrum arises from the phenomena of **spin coupling**. The theoretical origin of spin coupling is difficult to describe in a simple model, but arises because the nucleus undergoing resonance *senses* the spin of nearby NMR-active nuclei, and the orientation of these spins (parallel or antiparallel to the applied field) affects the chemical shift of the nucleus undergoing resonance. According to theory, this spin information is relayed to nearby nuclei through interactions with bonding electrons. For non-equivalent hydrogens on adjacent carbon atoms, this transfer occurs mostly through partial overlap of the electrons in the adjacent **CH** bonds.

Returning to the spectrum of diethyl ether (**Figure 4.5**), the three equivalent hydrogens on the terminal methyl group are adjacent to the two hydrogens on the methylene. The nuclei of these two hydrogens can have spins that are aligned with the applied field ($\uparrow\uparrow$), opposing the applied field ($\downarrow\downarrow$), or the two degenerate mixed orientations ($\uparrow\downarrow$ and $\downarrow\uparrow$). The presence of these nuclear dipoles on the adjacent carbon is sufficient to alter the chemical shift of the methyl nuclei so that resonance is observed at three different delta values, at relative integrations of 1:2:1 ($\uparrow\uparrow$, the degenerate pair $\uparrow\downarrow$ and $\downarrow\uparrow$ and $\downarrow\downarrow$). Operationally, the resonance of the methyl group has been split into $(n + 1)$ peaks, where n is the number of equivalent hydrogens on the adjacent carbon. This is referred to as the **$n + 1$ rule** and it states:

...the resonance from each magnetically distinct type of proton in a molecule will be split by adjacent, magnetically equivalent protons (n) into $(n + 1)$ components.

The rule can also be seen to apply to the methylene resonance. The methylene group is adjacent to the three equivalent methyl hydrogens (n is 3) and is therefore split into four $(n + 1)$ peaks. Commonly observed structures and their associated splitting patterns are collected in **Table 4-2**.

Table 4-2. Splitting patterns for common structural units.

Splitting, Integration		Splitting, Integration
doublet, area 1	$R_1-\overset{ }{\underset{ }{\text{CH}}}-\overset{ }{\underset{ }{\text{CH}}}-R_2$	doublet, area 1
doublet, area 2	$-\text{CH}_2-\overset{ }{\underset{ }{\text{CH}}}$	triplet, area 1
triplet, area 2	$R_1-\text{CH}_2-\text{CH}_2-R_2$	triplet, area 2
doublet, area 3	$\text{CH}_3-\overset{ }{\underset{ }{\text{CH}}}$	quartet, area 1
triplet, area 3	$\text{CH}_3-\text{CH}_2-R_2$	quartet, area 2
doublet, area 6	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}- \\ \\ \text{CH}_3 \end{array}$	septet, area 1
doublet, area 2	$\begin{array}{c} \text{H} & \text{H} \\ & \backslash & / \\ R_1- & \text{C} = \text{C} & -R_2 \\ & / & \backslash \\ \text{H} & \text{H} \end{array}$	doublet, area 2

A representative sample of an ethyl group, an isopropyl group, and an unsymmetrical 1,4-disubstituted benzene are shown below in **Figure 4.6**. Monosubstituted benzenes would be expected to be highly split since the ortho-, meta- and para-hydrogens are all nonequivalent. In practice, however, this depends on the exact nature of the substituent. For a simple alkyl group, the differences in chemical shift between these hydrogens are small and a singlet (or a slightly messy singlet) is commonly observed (**Figure 4.7 A**). At high field, however, this singlet is clearly shown to be the expected multiplet (**Figure 4.7 B**). Carbonyls adjacent to the ring will typically cause the ring hydrogens to couple, as will iodine and, to a lesser extent, bromine; chlorine, however, appears as a singlet at 60 MHz (**Figure 4.8**).

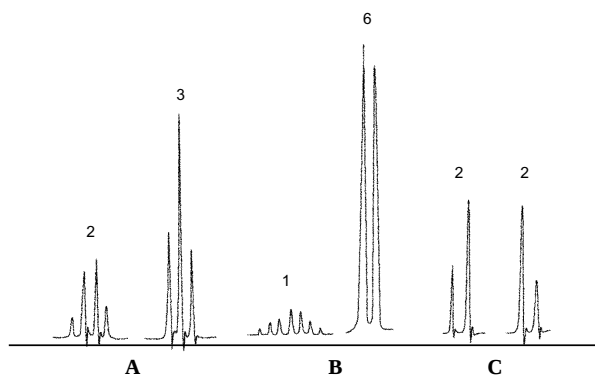


Figure 4.6 ^1H NMR showing a “typical” ethyl group (A), isopropyl group (B) and the pair of doublets observed in unsymmetrical 1,4-disubstituted benzenes..

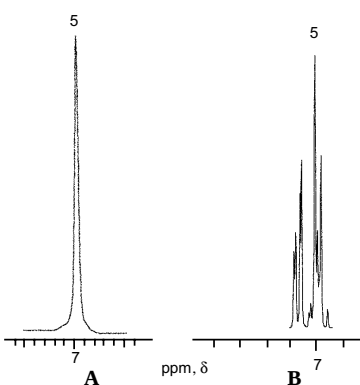


Figure 4.7 ^1H NMR showing the benzene ring hydrogens of toluene at 60 MHz (an apparent singlet) and at 300 MHz, where the non-equivalence of the ring hydrogens is apparent.

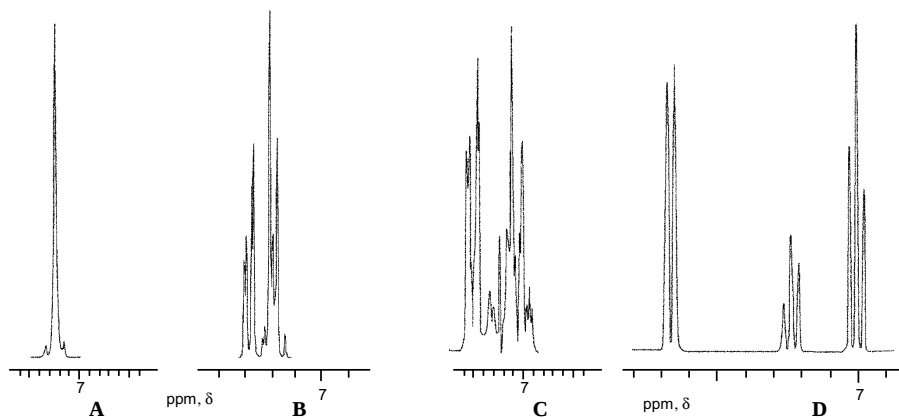


Figure 4.8 ^1H NMR showing the benzene ring hydrogens of chlorobenzene and iodobenzene at 60 MHz (A & C) and at 300 MHz (B & D), where the non-equivalence of the ring hydrogens is apparent.

The examples above also clearly demonstrate the enhanced resolution that is available with NMR spectrometers that function at higher frequencies (and higher magnetic field strength). The resolution is achieved because the coupling constant (in Hz) is directly dependent on the applied field, but the chemical shift is not (remember, the frequency cancels in the chemical shift equation). To achieve the required field strengths, cryogenic, super-conducting magnets are utilized, making the instruments expensive to obtain and to operate.

While the multiplicity of a resonance can be (roughly) predicted by the $n + 1$ rule, the intensity of each peak in the multiplet can be approximated by **Pascal's triangle**. In this mnemonic device, the relative areas for each multiplet are given across each row. Mathematically, the relative intensity for an entry in the table is given as the simple sum of the two bracketing entries in the row above it. Thus, for a septet (in an isopropyl group), the seven peaks will have relative intensities of 1, 6, 15, 20, 15, 6 and 1. The very small relative intensities of the first- and last peaks in the set often makes it difficult to accurately determine multiplicity, especially if there is significant background noise in the spectrum.

Pascal's Triangle

Singlet				1					
Doublet			1		1				
Triplet			1		2		1		
Quartet			1	3		3	1		
Quintet		1	4		6		4	1	
Sextet		1	5	10		10	5	1	
Septet	1	6	15		20		15	6	1

The Coupling Constant

The coupling constant, abbreviated as J , is simply the distance in Hz between the centers of peaks in a multiplet. The stronger the interaction between a nucleus and its neighboring nuclei, the larger the value of J . For coupling between hydrogens in common organic compounds, coupling constants generally vary within the range of 1 to 20 Hz, with small values being associated with geminal (or long-range) coupling and the larger values being characteristic of *trans* alkene hydrogens. Although the exact values of J vary with environment, **a pair of coupled nuclei will always have exactly the same coupling constant**; this is often useful in establishing nearest-neighbor relationships in a structure.

The identity of coupling interactions is often shown using subscripts on J ; for the alkene shown below, $J_{ab} \approx 2$ Hz, $J_{ac} \approx 17$ Hz and $J_{bc} \approx 10$ Hz. The striking difference between coupling constants *cis* and *trans* hydrogens (10 vs 17 Hz) is quite often useful in establishing stereochemistry in simple compounds. **Table 4-3** shows representative values for coupling constants observed in simple compounds.

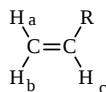
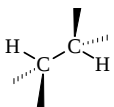
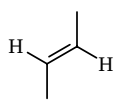
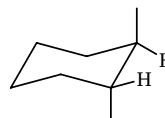
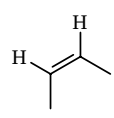
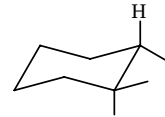
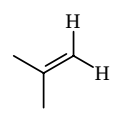
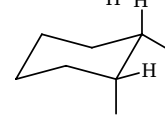
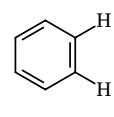


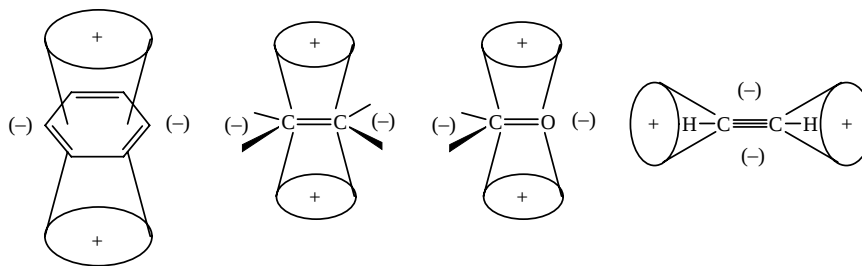
Table 4-3. Representative values for commonly observed coupling constants.

J , Hz		J , Hz	
	6 - 8		14 - 18
	0 - 5		6 - 12
	8 - 14		1 - 4
	0 - 7		6 - 10

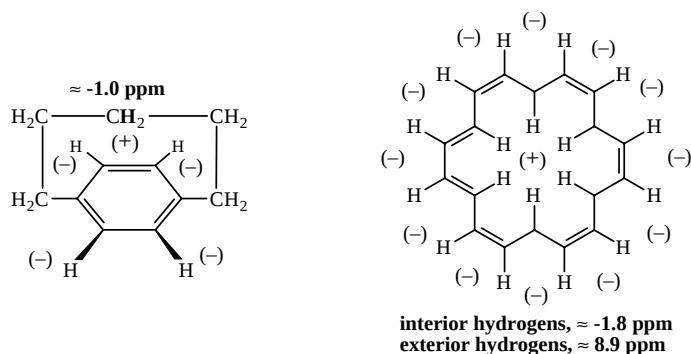
Magnetic Anisotropy

While simple electronegative arguments are sufficient to explain many observed chemical shifts, hydrogens which are bonded to multiply-bonded carbons are significantly deshielded (or shielded) to a greater extent than would be predicted, based on electronegativity alone. For example, hydrogens attached to benzene and its derivatives (and other **aromatic** compounds) reproducibly undergo resonance in the region 7 δ ppm, but a benzene ring (as a substituent) is no more electronegative than a simple carbonyl group. In aromatic compounds, the deshielding arises from the effect of a **ring current** in the aromatic π -system that is generated when the π -system is placed in the external magnetic field. This ring current generates a significant secondary magnetic field which opposes the applied field, resulting in an increase in the observed chemical shift. Because this secondary field is not uniform (i.e., it is anisotropic) shielding effects arising from these induced fields are referred to as arising from **magnetic anisotropy**.

All groups in a molecule which contain π -electrons generate anisotropic secondary fields in response to an external magnetic field. The lines-of-force in these fields can either shield or deshield hydrogens, depending on the exact shape of the field and the location of the particular hydrogen nucleus. General shapes of anisotropic fields for some simple functional groups are shown in (**Figure 4.9**). In these diagrams, protons within the (+) regions of space will be shielded and protons in the (-) regions will be deshielded.

**Figure 4.9** Anisotropic fields associated with common functional groups.

Conformation of this prediction is provided by the NMR spectra of *para*-cyclophane and 18-annulene. In *para*-cyclophane, the bridging methylene is held in the shielding portion of the field, while the ring hydrogens are normally deshielded, while in 18-annulene, the *interior* hydrogens are all held in the shielding cone, while the *exterior* hydrogens are deshielded.



Carbon (¹³C) NMR

The most abundant isotope of carbon is ¹²C, comprising about 98% of the natural abundance. Since this isotope has a spin of zero, it is not NMR-active and does not couple to NMR-active nuclei (such as ¹H), which would seriously complicate proton-NMR spectra. Carbon-13 (¹³C), however, has an odd mass and a spin of $I = 1/2$, meaning that it is NMR-active. Resonances from ¹³C are, however, difficult to observe, both because of the low natural abundance of the isotope and because the NMR-sensitivity of the ¹³C nucleus is low (in the ground state, there is a lower population of nuclei in the lower spin state than for hydrogen, making it more difficult to measure the spin-spin transition).

In spite of the technical difficulties, modern Fourier transform spectrometers make it possible to routinely study ¹³C NMR. To compensate for the low sensitivity of ¹³C, these instruments simply accumulate a large number of scans and then generate the average spectrum. As we will see, the sensitivity of the ¹³C spectrum can also be enhanced using *decoupling* techniques.

Chemical Shifts

As with protons, the frequencies at which carbon nuclei undergo resonance are a function of their electronic environment and can generally be related to neighboring functional groups. A simple correlation table showing common functional group effects is shown in **Figure 4.10**. These effects can be simply described as follows:

Simple *sp*³ Carbons. Simple unstrained and unhindered methyl and methylene carbons typically undergo resonance in the range **5 to 45 ppm**. Steric hindrance (secondary and tertiary centers) tend to be at the high end of this range, while terminal methyl groups tend toward the low end.

Carbons adjacent to Mildly Electronegative Groups. As before, the broad term *mildly electronegative* is used to include arenes, alkenes, alkynes, carbonyls, amines and sulfides. Carbons *adjacent* to these groups generally undergo resonance in the range **20 to 45 ppm**.

Carbons adjacent to Strongly Electronegative Groups. The broad term *strongly electronegative* is used to include halides, oxygen atoms, and nitro groups. Carbons *adjacent* to these groups generally undergo resonance in the range **30 to 60 ppm**.

Alkene Carbons. Alkene, sp^2 carbons typically undergo resonance in the range **100 to 140 ppm**, depending on substitution.

Arene Carbons. Arene (aromatic) ring carbons undergo resonance in the range **120 to 150 ppm**, depending on substitution.

Carbonyl Carbons. The carbons of aldehydes and ketones are the most highly deshielded carbons commonly encountered in organic chemistry and typically undergo resonance in the range **190 to 210 ppm**. This is well-separated from acyl compounds (acids, esters, amides, anhydrides and acid halides) which all tend to undergo resonance in the range **170 to 180 ppm**. The chemical shift of a carbonyl carbon therefore provides important information regarding functionality.

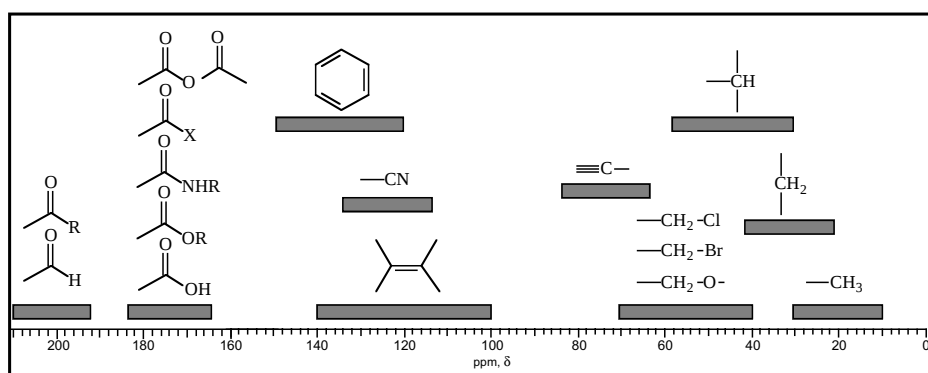


Figure 4.10 ^{13}C NMR chemical shifts of common functional groups.

Spin Coupling

As described previously for the ^1H NMR, adjacent ^{13}C nuclei would be expected to couple and to produce multiplets according to the $n + 1$ rule. The low natural abundance of ^{13}C , however, makes it highly unlikely that nearest neighbors will be NMR-active, and, in general, ^{13}C $\rightarrow$ ^{13}C coupling (homonuclear coupling) is not observed in unenriched compounds. It is, however, very likely that the ^{13}C carbons in a compound will be bonded to NMR-active hydrogens (^1H), and **splitting will therefore be observed between the ^{13}C nucleus and the attached hydrogens** (this is termed **heteronuclear coupling**). The multiplicity for this splitting follows the simple $n + 1$ rule; a CH_2 group will be split into a triplet (two hydrogens, three peaks), a CH_3 group into a quartet, carbonyls (except aldehydes) will be singlets, etc. You should note that splitting is **not observed** due to hydrogens on *neighboring carbons*, but rather arises from those hydrogens **directly attached to the carbon**.

Proton-Decoupled ^{13}C NMR Spectra

In spite of the fact that heteronuclear coupling is possible between ^{13}C and attached protons, the vast majority of ^{13}C spectra are obtained as **proton-decoupled** spectra. In decoupling, a second transmitter in the instrument is tuned to provide a broad spectrum of frequencies in the range where the ^1H nucleus undergoes resonance. The effect is to *saturate* the proton resonances so that only an average spin state of zero is observed, meaning that spin-spin coupling with the attached carbon is impossible. With the decoupler on, all resonances in the ^{13}C spectrum are reduced therefore to singlets. In the exercises in this book, ^{13}C NMR data will be provided with both chemical shift and multiplicity, although this information often is not available in the laboratory setting.

The reason that decoupling is routinely utilized in ^{13}C NMR is that the process of proton decoupling results in a significant enhancement in the observed ^{13}C NMR signal, allowing the sample to be processed much more quickly. This enhancement arises not only from the fact that multiplets now become singlets, but is largely due to what is called the **nuclear Overhauser enhancement (NOE)**.

The physical phenomena of the NOE for the ^{13}C D^1H system is an enhancement of the intensity of the ^{13}C resonance as a result of broad-frequency irradiation of the ^1H resonance. The origin of the effect lies in the fact that irradiation of the ^1H resonance saturates the proton spin states, and results in a non-equilibrium excess of nuclei in the *high-energy* spin state. The attached carbon nuclei respond to the non-equilibrium state by over-populating the *lower* spin state, resulting in more NMR-active nuclei, and a stronger resonance signal. The NOE effect is significant for the ^{13}C D^1H system, and at its maximum, the NOE will increase the signal strength by a factor of about two. Clearly, the more protons that are attached, the stronger the NOE and carbons without hydrogens will display no NOE; unfortunately the enhancement is not linear and the observed enhancement for each type of carbon varies significantly within most molecules.

Problems with Integration in ^{13}C NMR

In the proton NMR, the *intensity* of the NMR signal is directly proportional to the number of equivalent hydrogens giving rise to that signal. Theoretically, the same proportionality holds in ^{13}C NMR, although in practice, little useful information is generally available from the integration of ^{13}C spectra. The non-proportionality of signal intensity with equivalent sites in the molecule arises from two factors; the general practice of using proton decoupling to enhance the ^{13}C NMR signal and the fact that **relaxation** of carbon nuclei is generally slow, relative to the hydrogen nucleus. The first of these factors is quite simple; as described above, the NOE is variable within a molecule and enhancements will not directly parallel either the number of attached hydrogens, or the number of equivalent carbons giving rise to the signal. The integration of **non-decoupled** spectra is difficult, technically, because of the low signal strength and because of the fact that carbon nuclei *relax* from the excited state much more slowly than do hydrogen nuclei. As described previously, in FT-NMR nuclei are excited by a short RF pulse and the free induction decay (FID) wave-form is recorded and deconvoluted to provide frequency data for all relaxing nuclei. In order to obtain accurate intensity information for all nuclei, this FID must decay to essentially zero before the next RF pulse. With protons, the FID is generally complete in less than a second, allowing a rapid pulse sequence to be utilized and still capture accurate intensity information. Carbon nuclei, however, require several seconds, and sometimes several minutes, to relax. Experimentally, a pulse sequence which would capture accurate intensity information would require *extremely* long acquisition times, and is generally not done.

Chapter 5

INTEGRATED SPECTROSCOPY PROBLEMS

Students of organic chemistry often attempt to deduce the structure of an unknown compound utilizing only *one* spectroscopic method (usually NMR). If a simple spectrum does not provide enough data, higher resolution spectra are sought, or more advanced techniques are utilized (i.e., *two-dimensional* NMR). While these advanced techniques are powerful, and clearly extend the method, **the structures of most simple organic compounds can be easily deduced by the combined use of analytical data and simple, low resolution mass, infrared and NMR spectra.**

In the combined (or *integrated*) approach, each method is utilized to provide the information that it provides *best*. Infrared provides information regarding the *functional group* in a molecule. Mass spectrometry gives the *molecular weight* and tells you if certain easily recognizable structural fragments are present, ^{13}C NMR provides quick information on *symmetry* and on the different types of carbons in a molecule, and the splitting and chemical shifts in ^1H NMR provide details on the *constitution* of a molecule. For example, if the ^1H NMR of a compound shows only a triplet and a quartet, it is **screaming** at you, “ETHYL GROUP!”. And if this compound has a strong absorbance at 1720 cm^{-1} in the infrared... “CARBONYL!”. If the analysis is $\text{C}_5\text{H}_{10}\text{O}$, but only a three-line ^{13}C NMR is observed with a singlet at about 200 ppm, it **screams** “SYMMETRY” and “KETONE CARBONYL!”. Finally, if a molecular ion at $m/e = 86$ is observed in the mass spectrum (“MOLECULAR WEIGHT = 86”), the compound **must** be **diethyl ketone** (3-propanone).

In the following pages there are analytical data, and infrared, mass ^1H and ^{13}C NMR spectra for one hundred simple organic compounds. For the last fifty compounds, synthetic or qualitative analysis data (Tollens test, etc.) are generally provided, along with the spectroscopic data. While some are more challenging than others, the structures of all of these can be readily deduced by using the method of combined, or *integrated* spectroscopic analysis. Let’s review, briefly from the preceding chapters.

The Mass Spectrum

Use the **molecular ion** in the mass spectrum to determine the **molecular weight** and the nature of any **halogen** substitution. Remember that a compound containing bromine will show **two molecular ions of equal intensity**, and will have an ($m_{\text{average}} - 80$) peak in the spectrum. A compound containing chlorine will have **two molecular ions in the ratio 3 : 1** and will have an ($m_{\text{average}} - 35.5$) peak in the spectrum. Note the presence of *noteworthy* ions; **tropylium** ($m/e = 91$) **acylium** ($m/e = 43$), and the loss of standard fragments; methyl groups ($m - 15$), ethyl groups ($m - 29$), etc. Consult the table of **Common Fragments** in **Chapter 2** (page 28) for other simple cleavage products.

The Analysis

The percent compositions should be converted to empirical formulas. Use the molecular weight from the mass spectrum to convert the empirical formula into a molecular formula and calculate *degrees of unsaturation*. Remember that four or more degrees of unsaturation in a simple compound strongly suggests a benzene ring is present, while an unsaturation number of 1 – 3 suggests rings, carbonyls, and double or triple bonds may be present. Review the rules for calculating unsaturation numbers for compounds containing heteroatoms (oxygen, nitrogen and halogens) from **Chapter 1**.

The Infrared Spectrum

The infrared spectrum provides both positive and negative data regarding functional groups. For example, a compound containing oxygen with no peak at 3400 cm^{-1} and no peak at $\approx 1720\text{ cm}^{-1}$ is neither an alcohol nor does it contain a carbonyl, and is quite possibly an ether. Therefore, it is useful to march through the standard set of characteristic absorbance bands, noting their presence or absence:

- $\approx 3400\text{ cm}^{-1}$: O–H and N–H stretch (alcohols and amines); strong, broad and reliable,
- $\approx 3100\text{ cm}^{-1}$: sp and sp^2 C–H stretch (alkynes, alkenes and arenes); medium intensity, moderate utility,
- $\approx 2900\text{ cm}^{-1}$: sp^3 C–H stretch (saturated carbon); medium to strong, moderately informative,
- $\approx 2750\text{ cm}^{-1}$: aldehyde C–H stretch; medium intensity, useful because not much else absorbs in this region
- $\approx 2200\text{ cm}^{-1}$: C≡C and C≡N stretch (alkynes and nitriles); medium intensity, sharp, useful for nitriles, but may be very weak for alkynes,
- $\approx 1700\text{ cm}^{-1}$: the C=O stretch; strong, broad and one of the most diagnostic peaks in the infrared spectrum,
- $\approx 1600\text{ cm}^{-1}$: the C=C stretch (alkenes and arenes); medium intensity, sharp and moderate utility; arenes typically display 2 – 4 sharp bands in the region $1600 - 1450\text{ cm}^{-1}$,
- $\approx 1200\text{ cm}^{-1}$: the C–O stretch; strong, broad, but of limited utility because many other things also absorb in this region.

While these are the most “reliable” or (at least) *useful* infrared bands, you should review **Chapter 3** for a more complete discussion of *other* characteristic absorbances.

The ^1H NMR Spectrum

In its simplest form, the proton NMR tells you three things:

- the **electronic environment** of the protons in the molecule (from the **chemical shift**),
- the **relative numbers** of each type of magnetically distinct protons in the molecule (from the **integration**), and,
- the number of **magnetically equivalent protons that are adjacent** to the proton undergoing resonance (from the splitting).

As you look at a proton NMR, you should first rank resonances according to environment, by chemical shift. Remember the basic regions:

- 0.5 – 1.5 ppm:** *simple* alkane hydrogens (also cyclopropanes),
- 2.0 – 3.0 ppm:** hydrogens on carbons that are adjacent to a *mildly electronegative group* (carbonyls, halogens, benzene rings),
- 3.0 – 4.5 ppm:** hydrogens on carbons that are adjacent to a *strongly electronegative group* (typically oxygens, or multiple halogens, multiple carbonyls, etc.),
- 5.0 – 6.5 ppm:** alkene hydrogens,
- 7.0 – 8.5 ppm:** arene hydrogens,
- 9.0 – 10 ppm:** the aldehyde C–H,
- 11 – 12 ppm:** the carboxylic acid O–H.

Next, you should examine the splitting patterns, looking first for standard sets such as the ethyl group (a triplet and a quartet), the isopropyl group (a doublet and a septet) and a set of doublets in the arene region (unsymmetrical, 1,4-disubstituted benzenes). Also note singlets as *isolated* methyl or methylene groups (use the integration) and singlets or sharp multiplets in the arene region as mono- or poly-substituted benzenes (again, use the integration). Finally, ponder over any more complex splitting that may be present, using the ($n + 1$) rule to pair coupled hydrogens.

The ^{13}C NMR Spectrum

In its simplest form, the carbon NMR tells you three things:

- the **electronic environment** of the carbons in the molecule (from the **chemical shift**),
- the **number of magnetically distinct carbons in the molecule** (from the **number of peaks**), and,
- the number of **magnetically equivalent protons that are bonded to** the carbon undergoing resonance (from the splitting).

As you look at a carbon NMR, again, you should first rank resonances according to environment, by chemical shift. Remember the basic regions:

- 10 – 30 ppm:** *simple* alkane carbons (steric crowding will increase the chemical shift),
- 40 – 60 ppm:** carbons that are adjacent to a **mildly electronegative group** (carbonyls and halogens),
- 60 – 80 ppm:** carbons that are adjacent to a **strongly electronegative group** (typically oxygens, or multiple halogens, multiple carbonyls, etc.),
- 100 – 140 ppm:** **alkene** carbons,
- 120 – 150 ppm:** **arene** carbons,
- 150 – 160 ppm:** **nitrile** carbons,
- 165 – 180 ppm:** **carbonyls from acyl derivatives** (carboxylic acids, acid halides, esters, amides and anhydrides),
- $\approx$ 200 ppm:** **ketone and aldehyde carbonyls** (remember that aldehydes will be **doublets**).

Next, you should examine the splitting patterns, ranking each carbon as a methyl group (a **quartet**), a methylene (a **triplet**), a C–H (a **doublet**) or an *isolated carbon* that is not bonded to any hydrogens (a **singlet**). Finally, look at the total number of peaks in the carbon-NMR and compare this with the total number of carbons in the molecular formula; if there are fewer peaks than there are carbons, the molecule must have symmetry elements (two magnetically identical ethyl groups, etc.).

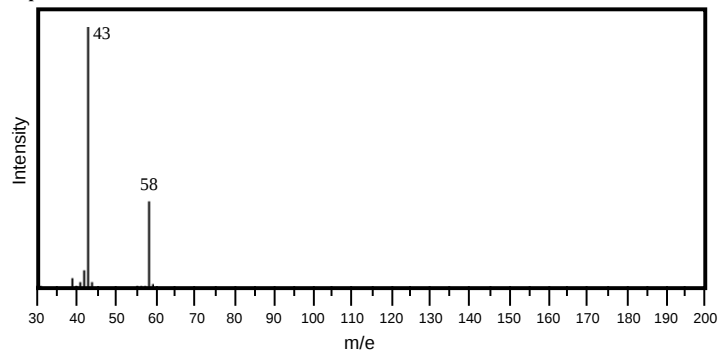
Put the Pieces Together

To draw the structure of the compound, simply note each of the structural elements you obtained from each spectroscopic method. In general, once the *pieces* are defined, there is only one way to link them together into a consistent chemical structure.

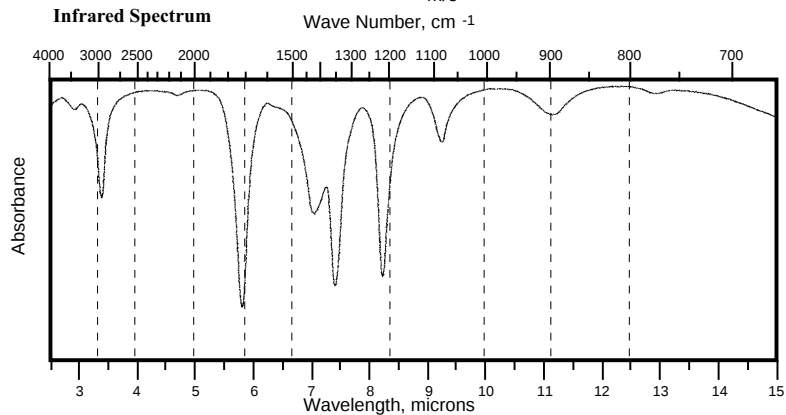
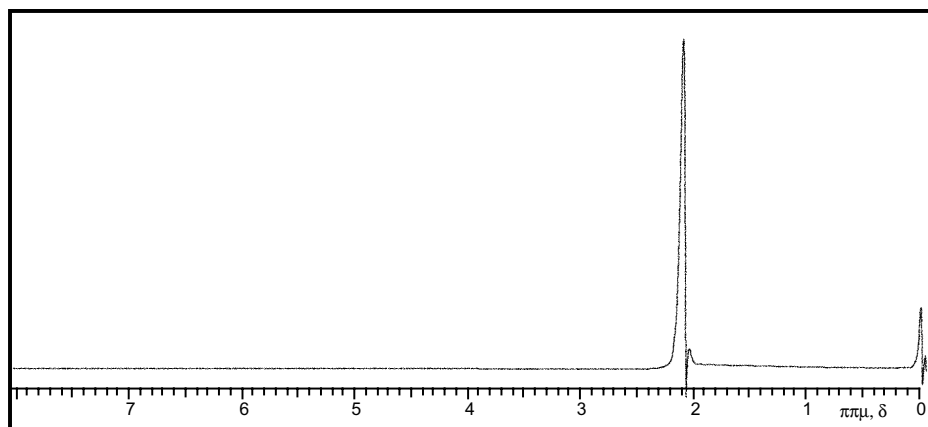
Each of the spectroscopy problems in the set that follows is also on the accompanying CD in tutorial format, which should be utilized as real-time help in the analysis process, or as a method for checking your logic and verifying the correct structures.

Compound 1 is a volatile liquid (boiling point 56°C) that is used as a common organic solvent. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 62.04; H, 10.41; O, 27.55

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

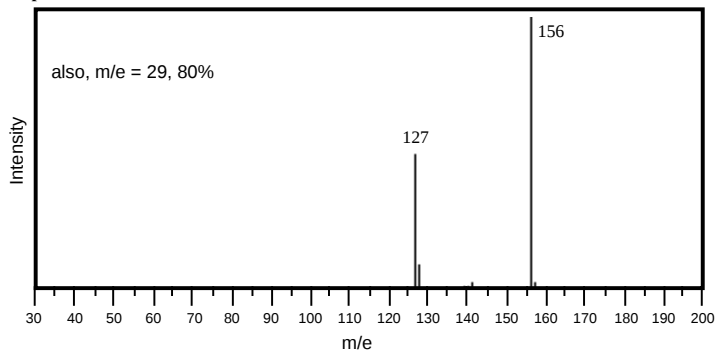
singlet, 206.0 ppm;
quartet, 27.0 ppm

Structure:

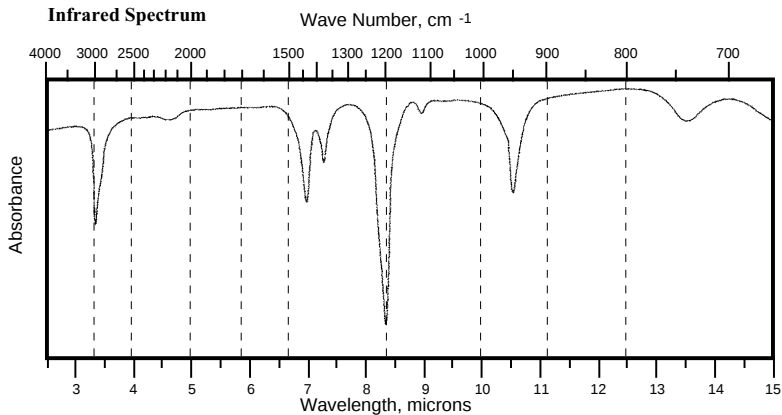
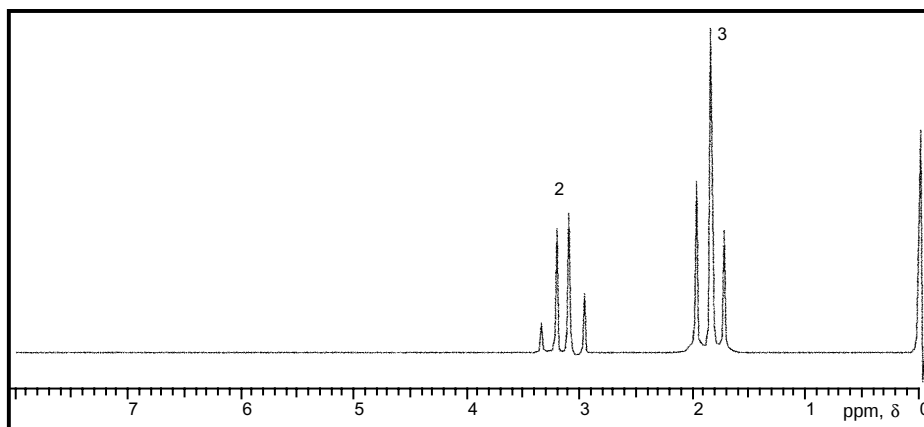


Compound 2 is a liquid (boiling point 72°C), that reacts with alkoxide to yield an ether. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 15.40; H, 3.23; contains halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

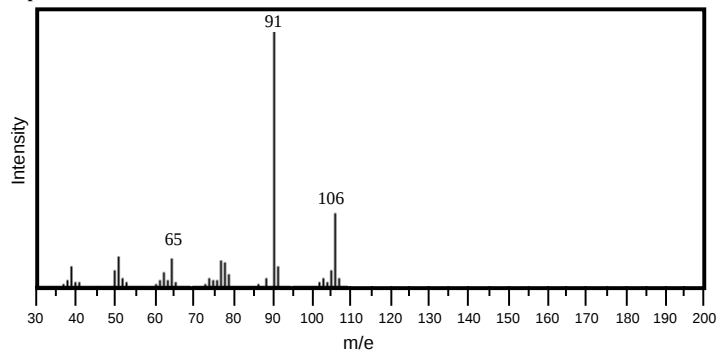
quartet, 17.7 ppm;
triplet, 0.4 ppm

Structure:

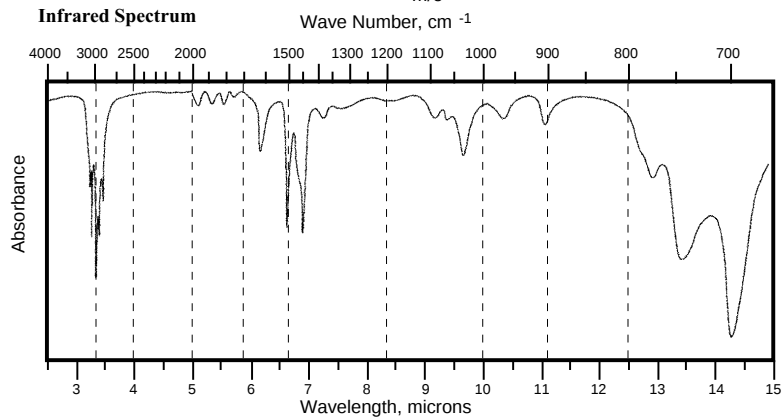
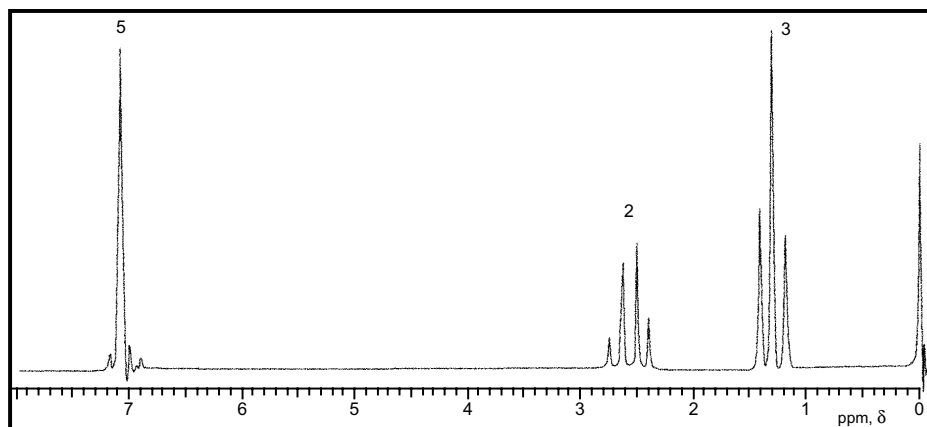


Compound 3 is a liquid, boiling point 136 °C. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below.
Elemental Analysis: C, 90.51; H, 9.49.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

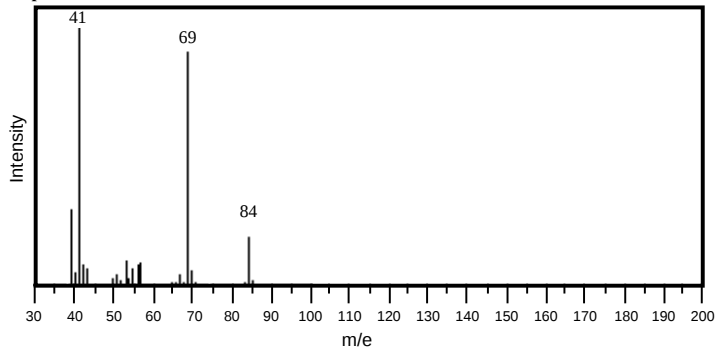
singlet, 140.2 ppm
 doublet, 128.4 ppm
 doublet, 127.9 ppm
 doublet, 125.7 ppm
 triplet, 31.1 ppm
 quartet, 16.1 ppm

Structure:

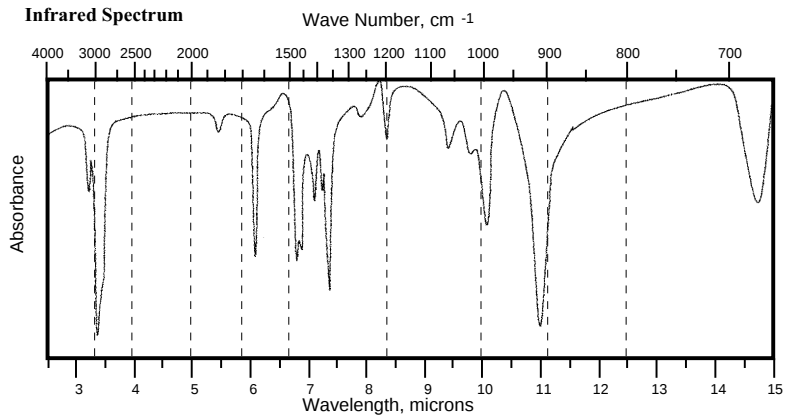
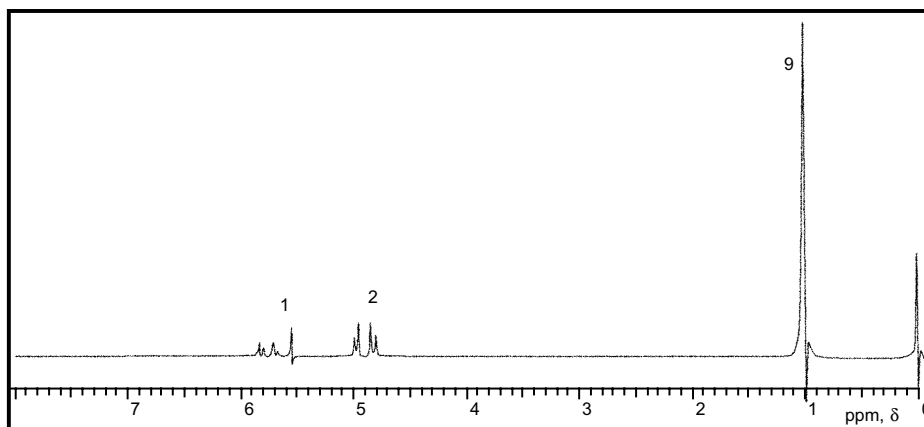


Compound 4 is a low-boiling hydrocarbon (boiling point 41°C), that reacts with bromine in CCl_4 to yield a 1,2-dibromide. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 85.63; H, 14.37.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

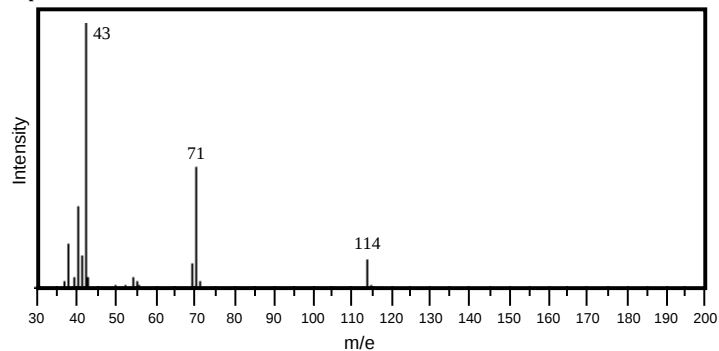
doublet, 149.3 ppm;
triplet, 108.5 ppm;
singlet, 44.5 ppm;
quartet, 33.6 ppm

Structure:

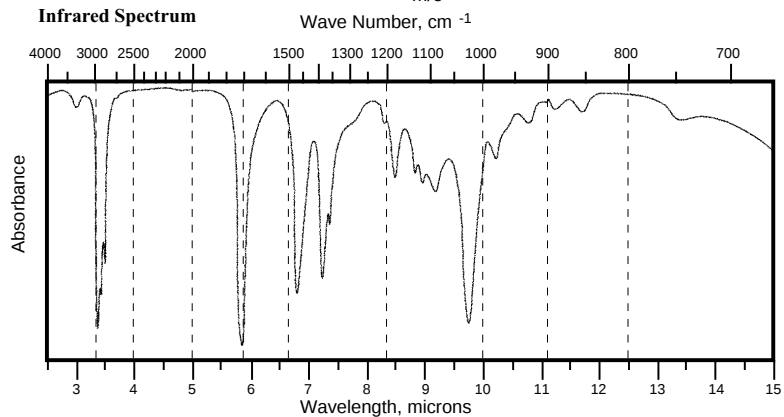
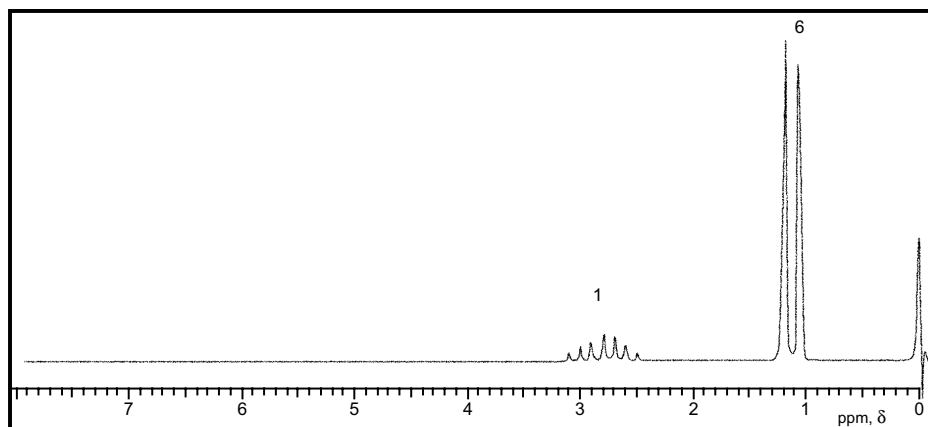


Compound 5 is a liquid, boiling point 124°C. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below.
Elemental Analysis: C, 73.63; H, 12.36; O, 14.01.

Mass Spectrum



Infrared Spectrum

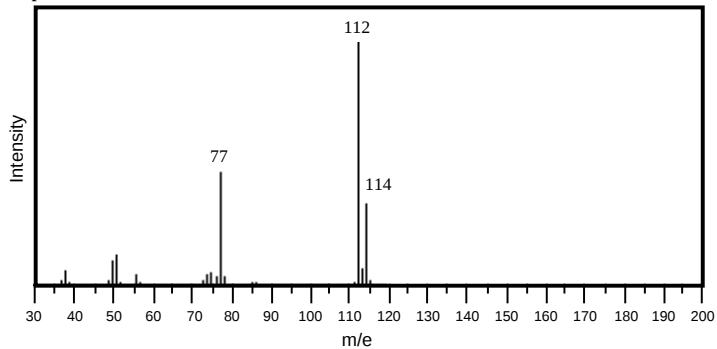
 ^1H NMR **^{13}C Spectral Data:**

singlet, 214.4 ppm
 doublet, 40.2 ppm
 quartet, 17.3 ppm

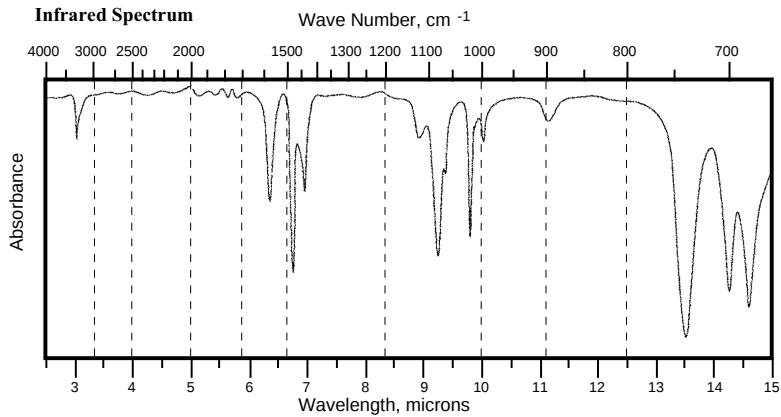
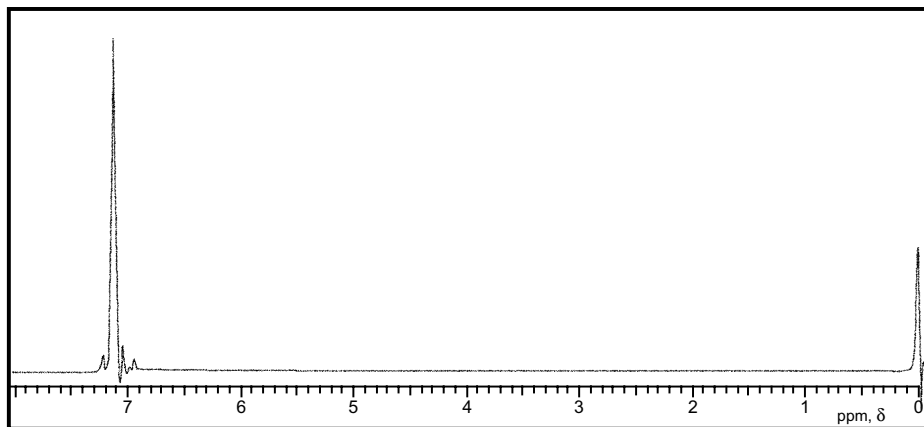
Structure:

Compound 6 is a liquid, boiling point 130°C. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. Elemental Analysis: C, 64.02; H, 4.48; contains halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

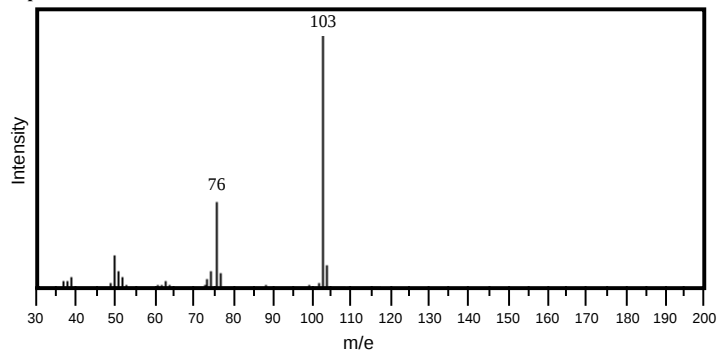
singlet, 133.8 ppm
doublet, 129.9 ppm
doublet, 128.9 ppm
doublet, 126.6 ppm

Structure:

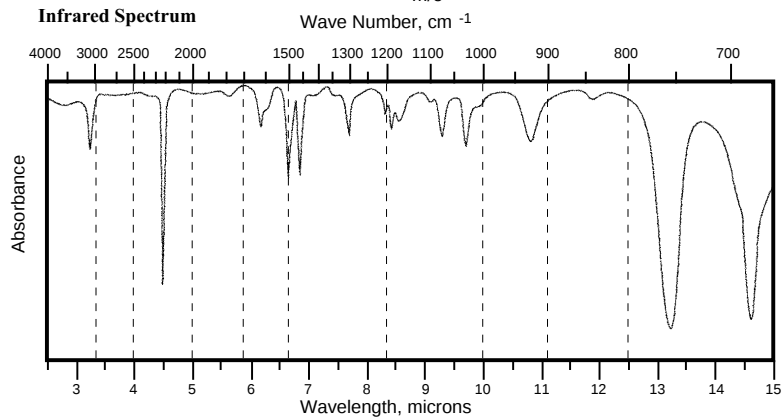
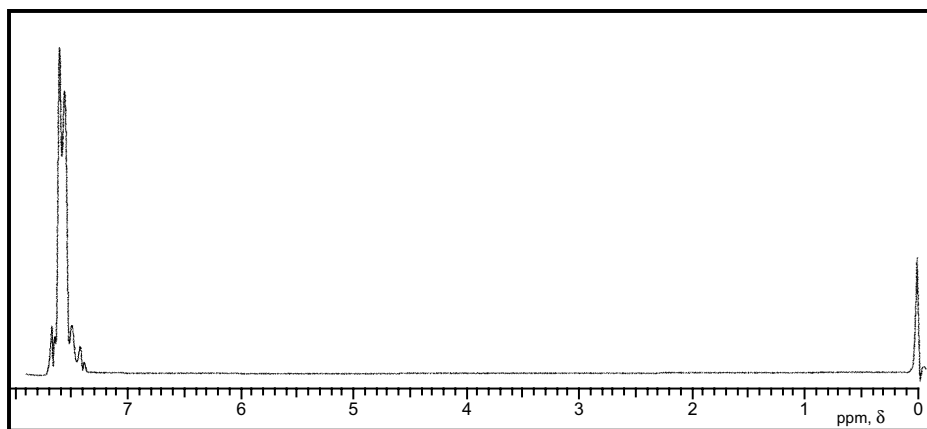


Compound 7 is a high-boiling liquid (boiling point 191°C). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 81.53; H, 4.89; N, 13.58.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

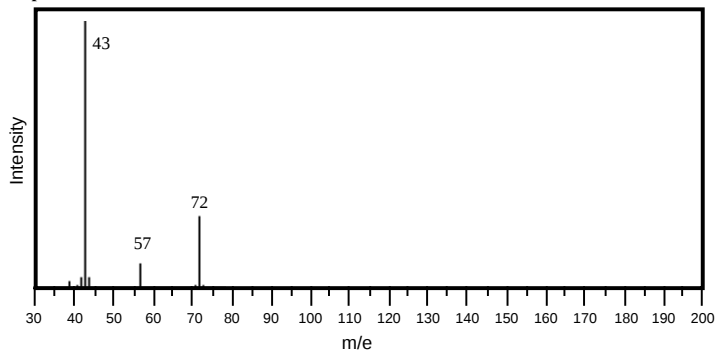
doublet, 132.8 ppm
doublet, 132.0 ppm
doublet, 129.2 ppm
singlet, 116.5 ppm
singlet, 112.5 ppm

Structure:

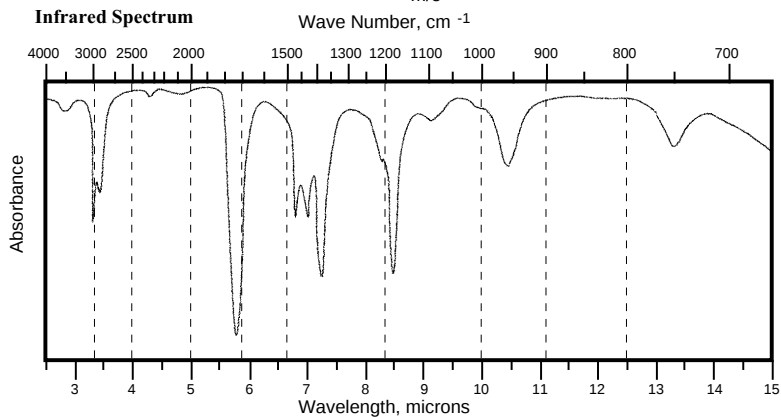
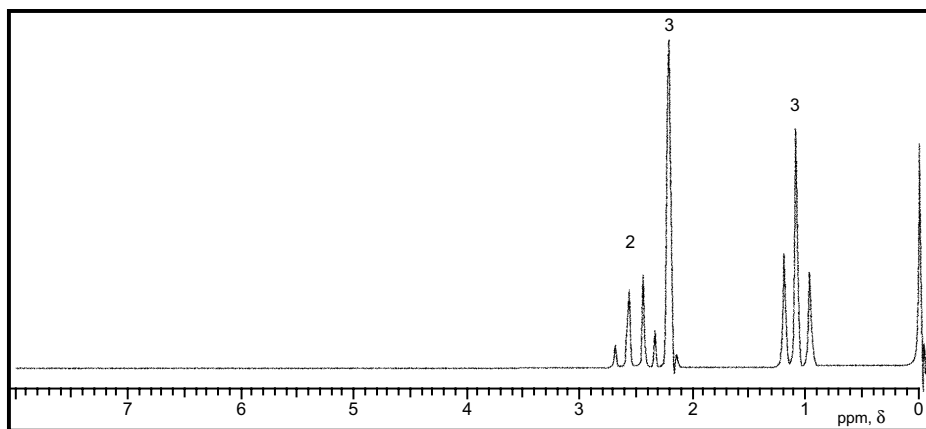


Compound 8 is a volatile liquid (boiling point 79.6°C), that is used as a common organic solvent. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 66.63; H, 11.18; O, 22.19.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

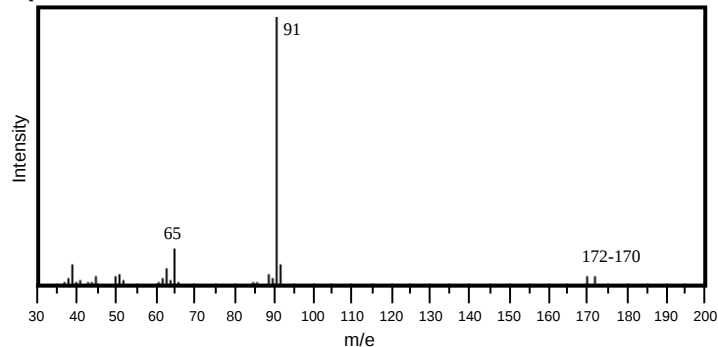
singlet, 207.1 ppm
triplet, 36.1 ppm
quartet, 24.5 ppm
quartet, 7.3 ppm

Structure:

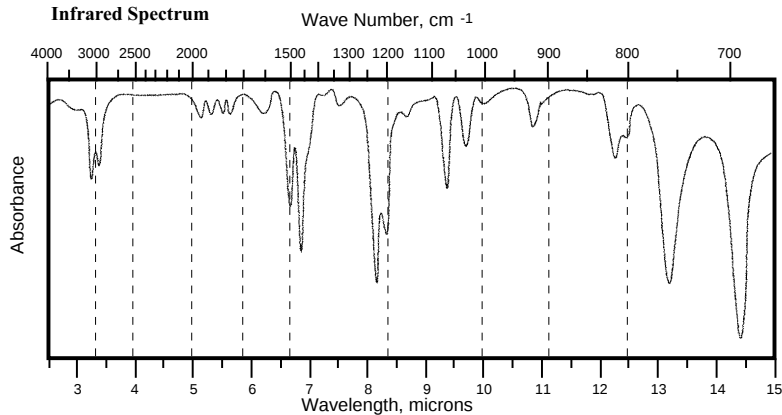
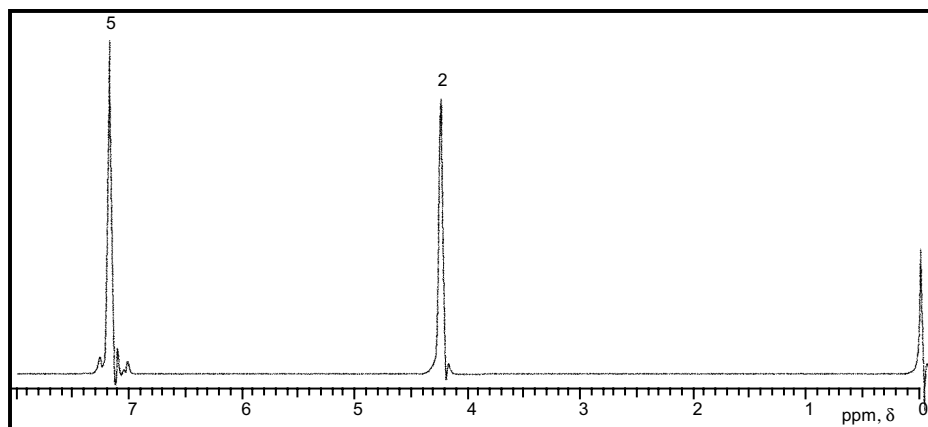


Compound 9 is a high-boiling liquid (boiling point 201°C), that reacts with alkoxide to yield an ether. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 49.16; H, 4.13; contains halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

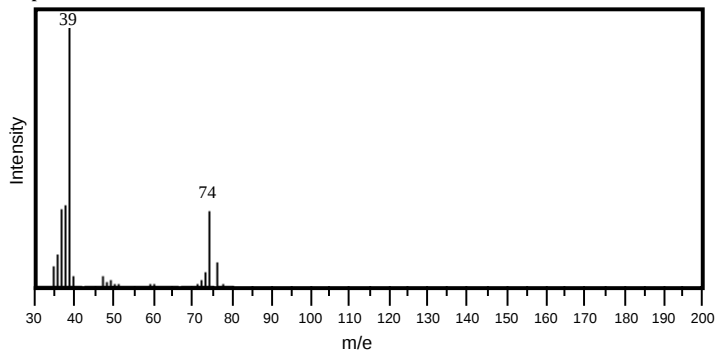
singlet, 130.1 ppm;
doublet, 129.0 ppm;
doublet, 127.8 ppm;
doublet, 127.7 ppm;
triplet, 29.3 ppm

Structure:

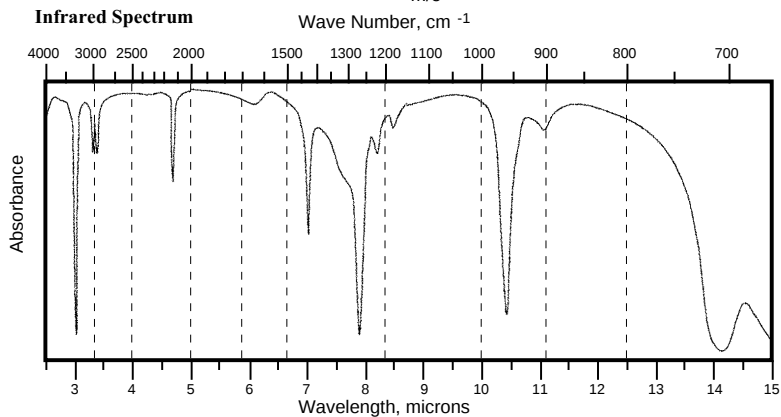
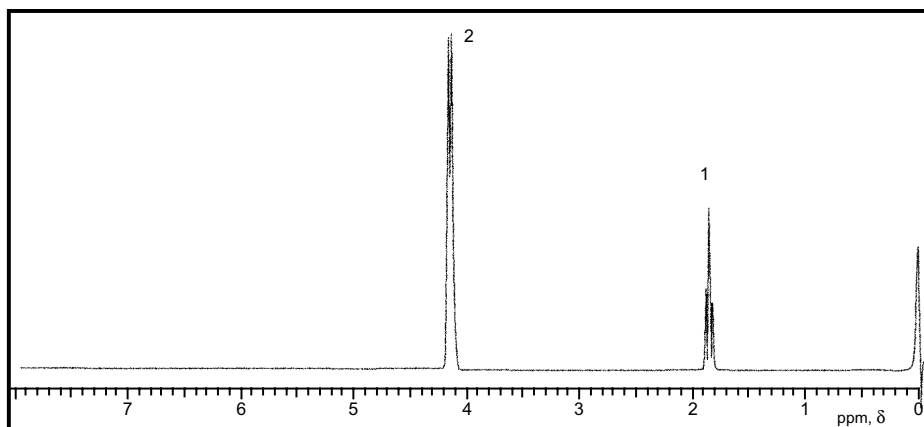


Compound 10 is a low-boiling liquid (boiling point 58 °C), that reacts with Br₂ in CCl₄ to form a 1,1,2,2-tetra bromide. The Mass, IR, and ¹H NMR spectra, along with ¹³C NMR data, are given below. **Elemental Analysis:** C, 48.36; H, 4.06; contains halogen.

Mass Spectrum



Infrared Spectrum

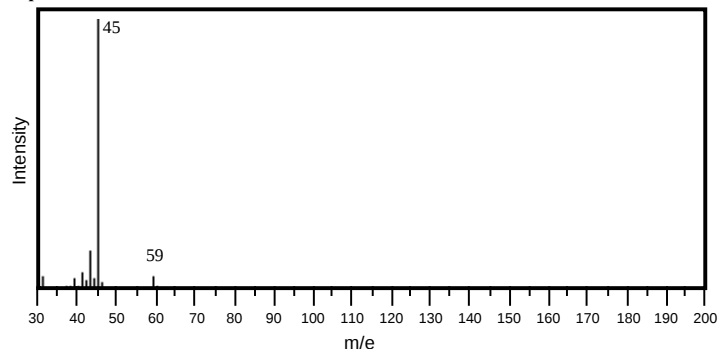
¹H NMR**¹³C Spectral Data:**

doublet, 80.4 ppm
singlet, 68.3 ppm
triplet, 34.7 ppm

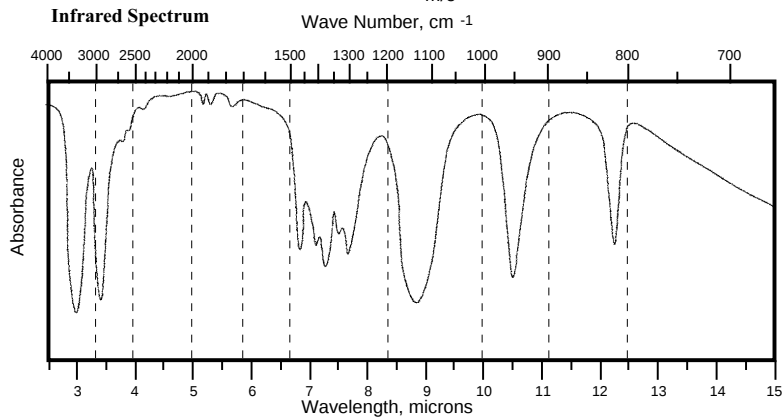
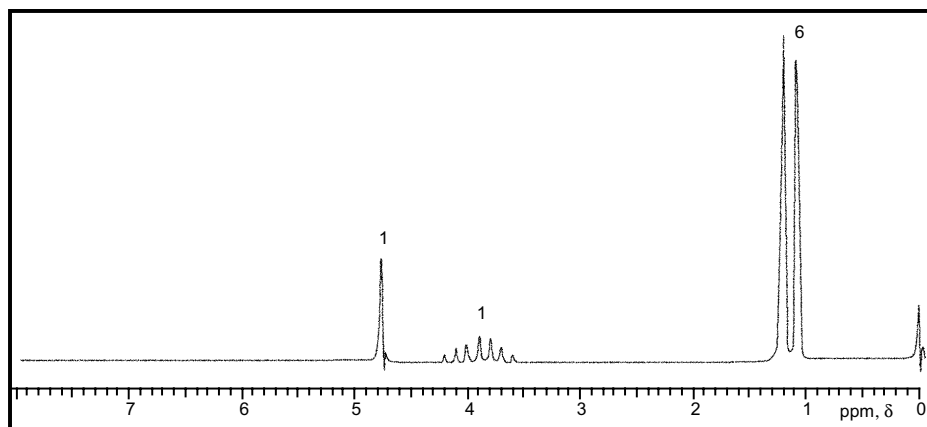
Structure:

Compound 11 is a volatile liquid (boiling point 82° C) that is fully miscible with water. The peak at 4.8 ppm in the ^1H NMR disappears if the compound is exposed to D_2O ; the molecular ion ($m/e = 60$) does not appear in the mass spectrum of this compound. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 59.96; H, 13.42; O, 26.62.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

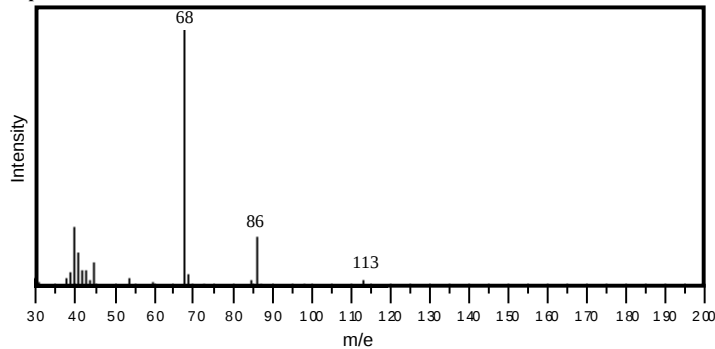
doublet, 64.9 ppm;
quartet, 26.3 ppm

Structure:

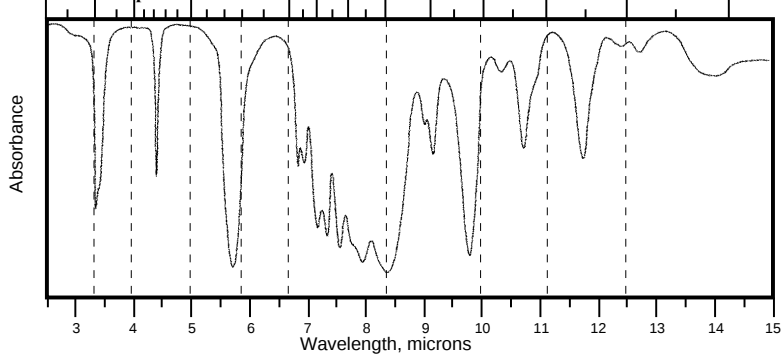
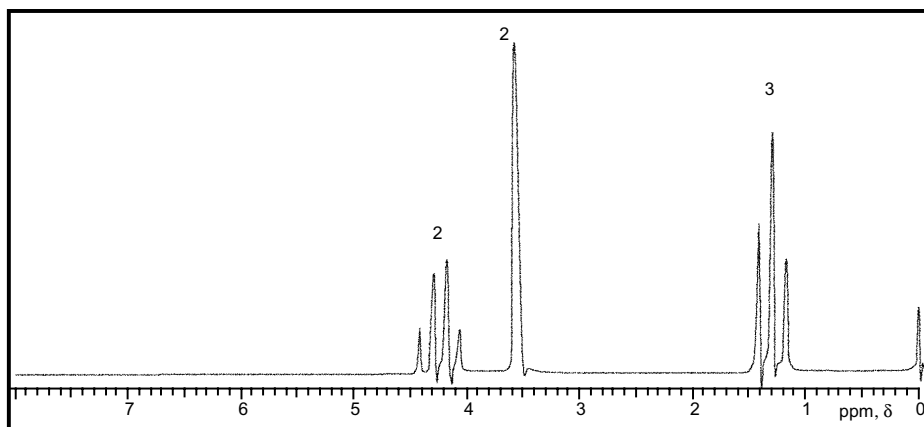


Compound 12 is a high-boiling neutral liquid (boiling point 206° C). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 82.02; H, 6.02; N, 11.96.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

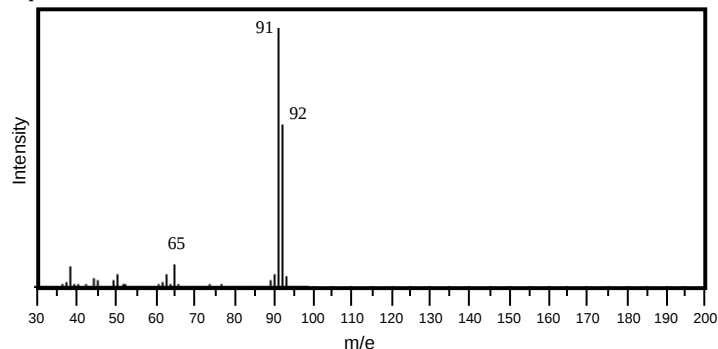
singlet, 172.0 ppm;
singlet, 117.7 ppm;
triplet, 58.7 ppm;
triplet, 21.6 ppm;
quartet, 13.6 ppm

Structure:

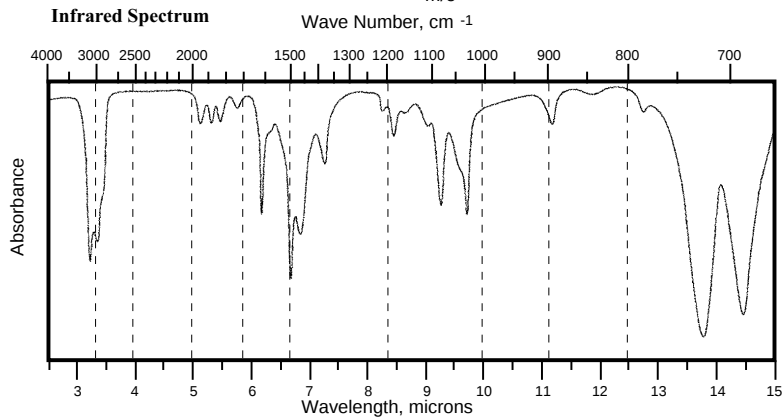
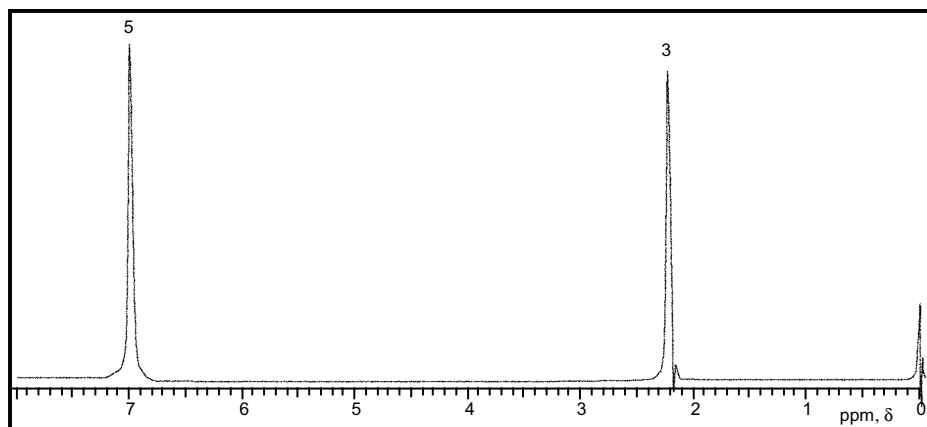


Compound 13 is a liquid (boiling point 110° C) that is often used as an organic solvent. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 91.25; H, 8.75

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

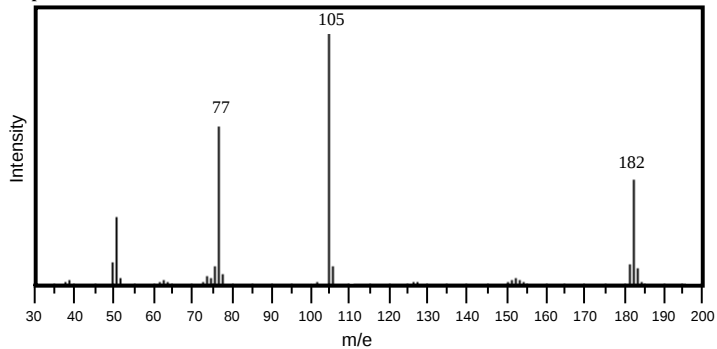
singlet, 137.7 ppm;
doublet, 129.2 ppm;
doublet, 128.4 ppm;
doublet, 125.5 ppm;
quartet, 22.0 ppm

Structure:

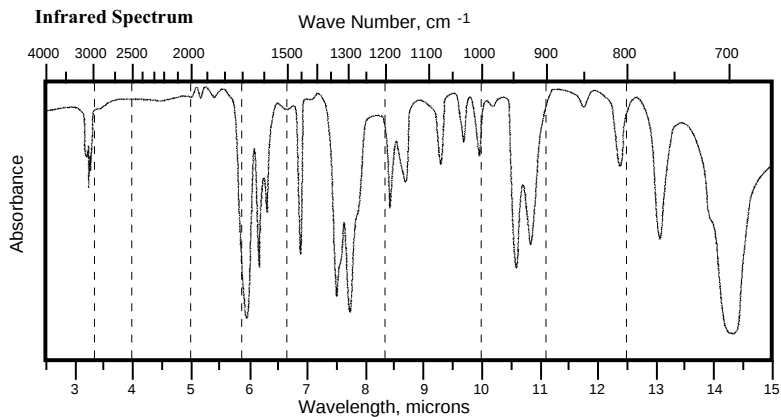
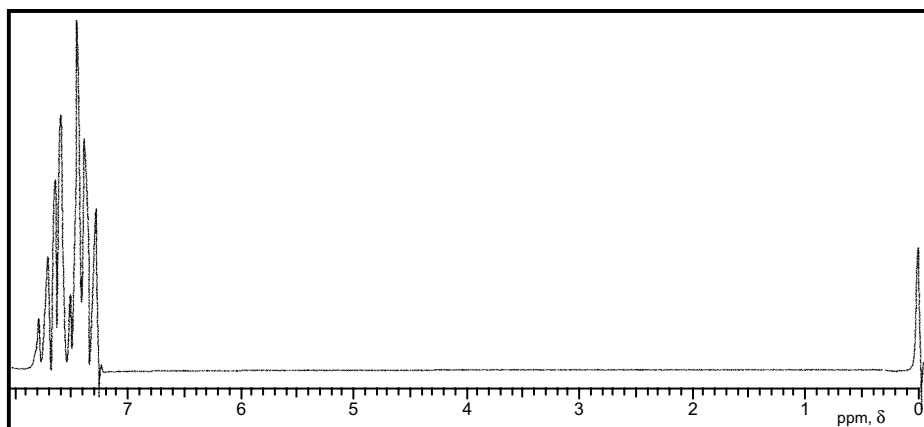


Compound 14 is a low-melting solid (melting point 48–49 °C). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 85.69; H, 5.53; O, 8.78.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

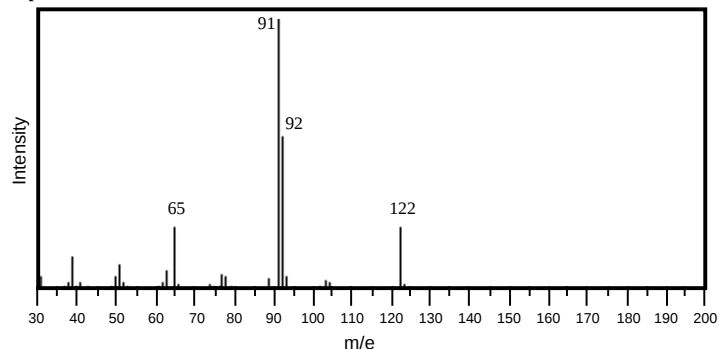
singlet, 187.0 ppm
singlet, 137.8 ppm
doublet, 132.2 ppm
doublet, 130.1 ppm
doublet, 128.2 ppm

Structure:

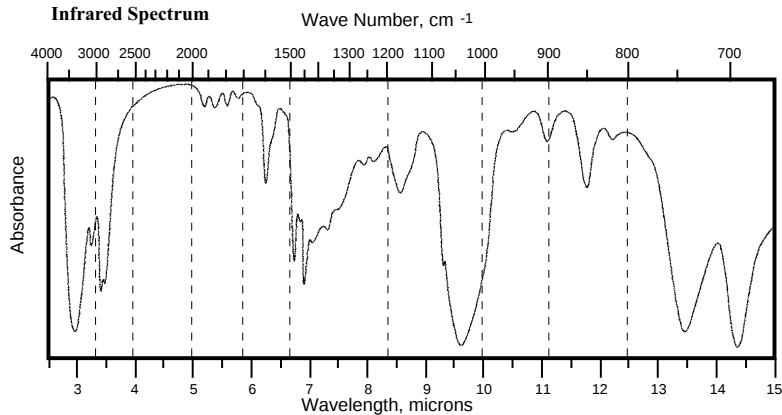
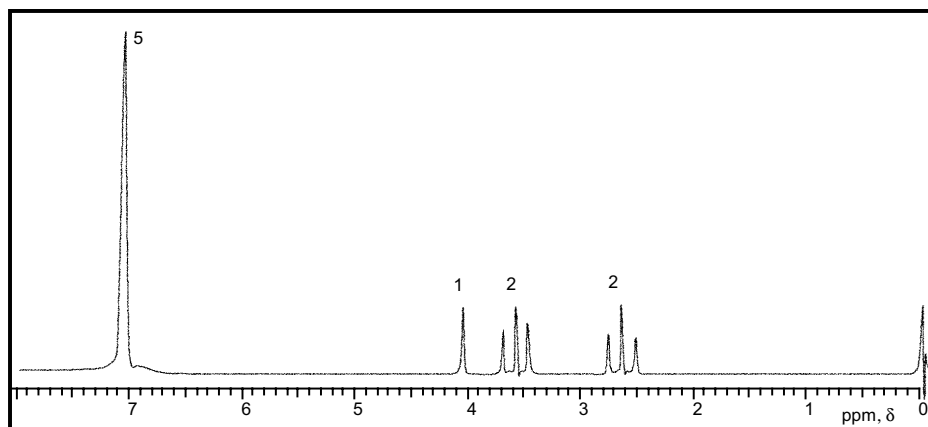


Compound 15 is a high-boiling liquid (boiling point 220° C) that is slightly soluble in water.. The peak at 4.15 ppm in the ^1H NMR disappears if the compound is exposed to D_2O . The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below.
Elemental Analysis: C, 78.65; H, 8.25; O, 13.10.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

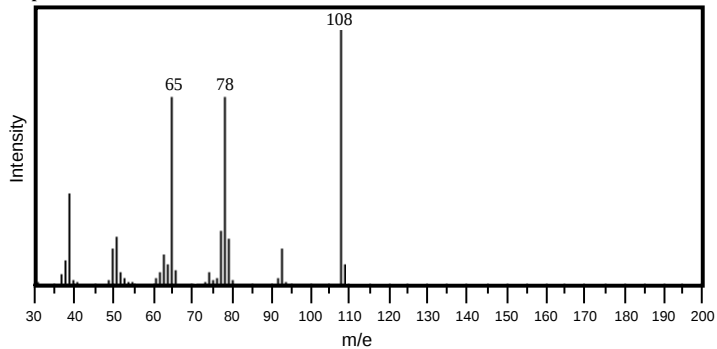
singlet, 140.2 ppm;
 doublet, 128.4 ppm;
 doublet, 127.9 ppm;
 doublet, 125.7 ppm;
 triplet, 68.5 ppm;
 triplet, 44.6 ppm

Structure:

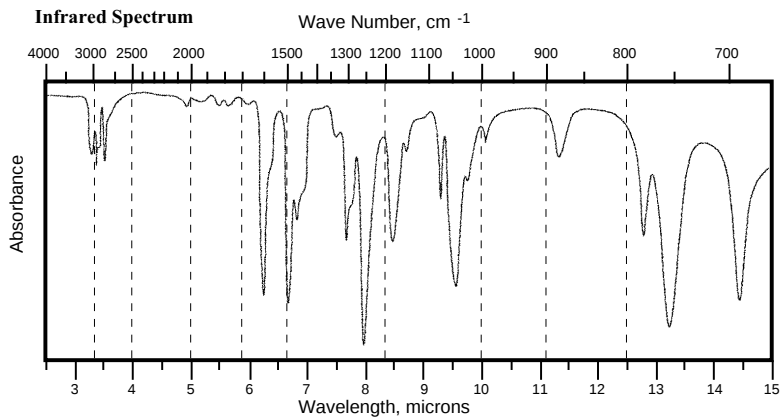
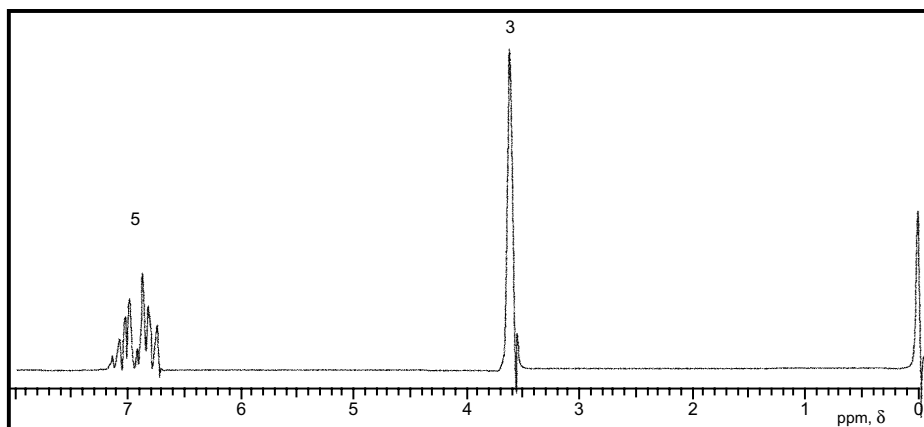


Compound 16 is a neutral liquid, boiling point 152 °C. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 77.75; H, 7.46; O, 14.80.

Mass Spectrum



Infrared Spectrum

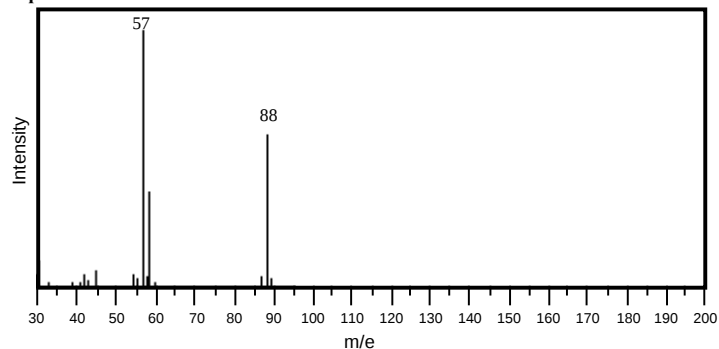
 ^1H NMR **^{13}C Spectral Data:**

singlet, 162.0 ppm
doublet, 129.5 ppm
doublet, 120.8 ppm
doublet, 114.1 ppm
quartet, 56.0 ppm

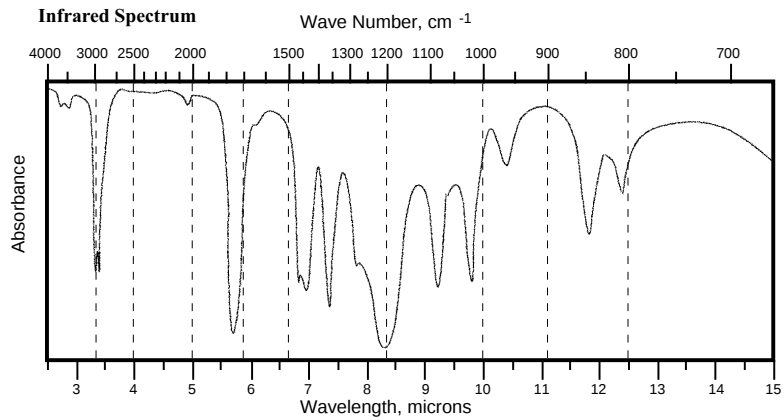
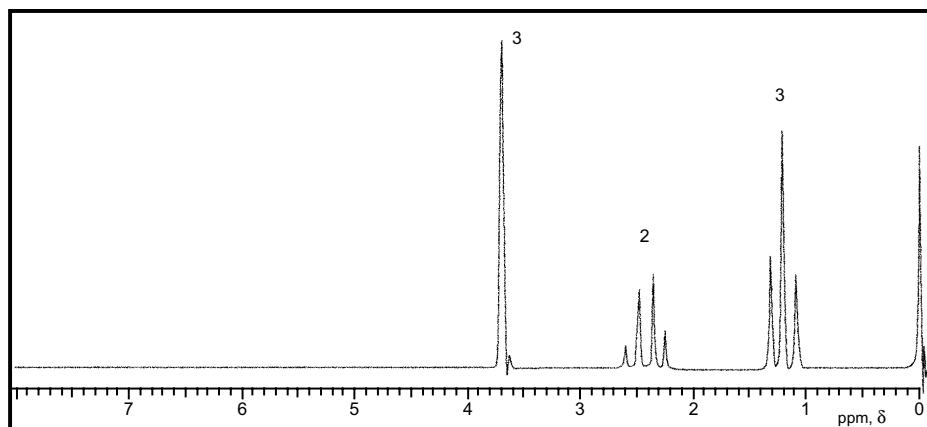
Structure:

Compound 17 is a sweet-smelling liquid, boiling point 80 °C. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 54.53; H, 9.15; O, 36.32.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

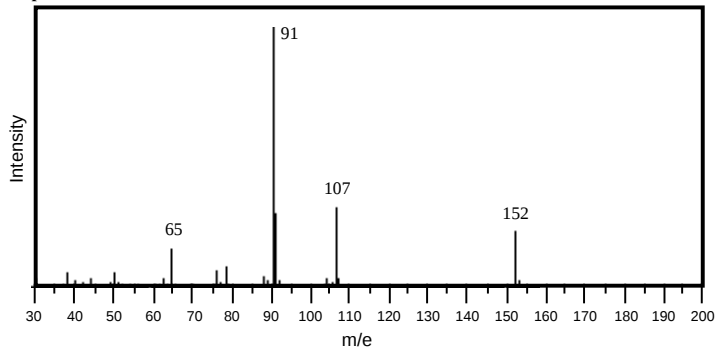
singlet, 172.0 ppm
 quartet, 50.4 ppm
 triplet, 26.1 ppm
 quartet, 9.1 ppm

Structure:

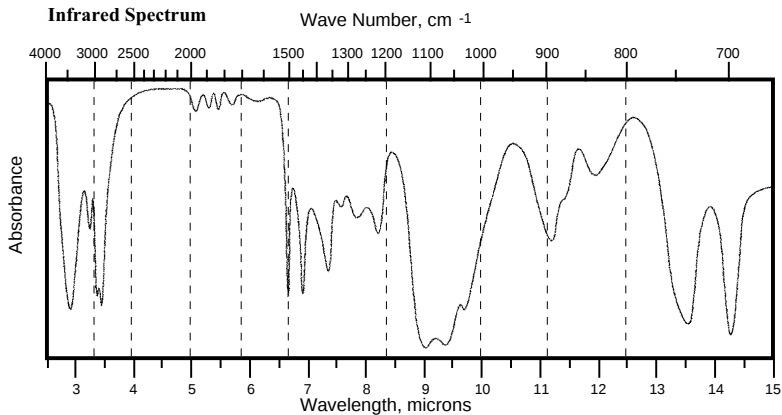
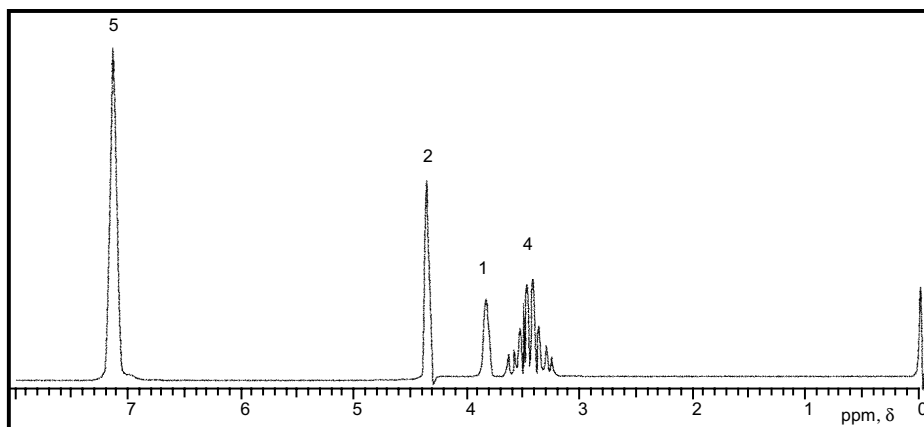


Compound 18 is a high-boiling liquid (boiling point 256° C) which is slightly soluble in water. The peak at 3.9 ppm in the ^1H NMR disappears if the compound is exposed to D_2O . The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 71.03; H, 7.95; O, 21.03.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

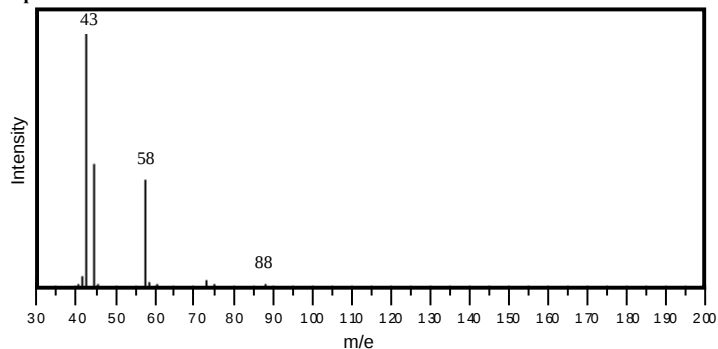
singlet, 137.2 ppm;
doublet, 128.4 ppm;
doublet, 127.6 ppm;
doublet, 127.5 ppm;
triplet, 81.6 ppm;
triplet, 79.5 ppm;
triplet, 67.1 ppm

Structure:

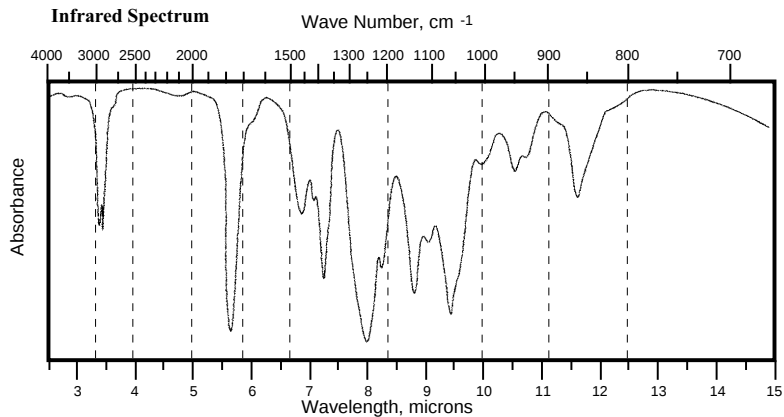
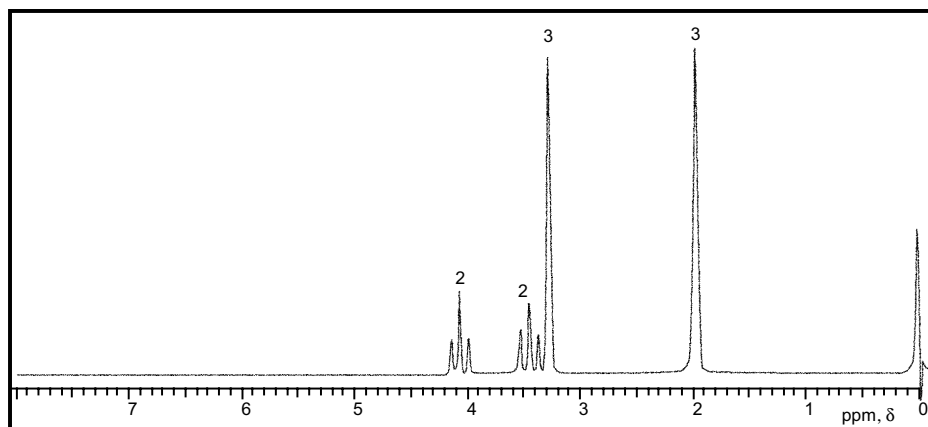


Compound 19 is a liquid (boiling point 143° C) that undergoes hydrolysis to form a neutral compound and a carboxylic acid. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 50.84; H, 8.53; O, 40.63.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

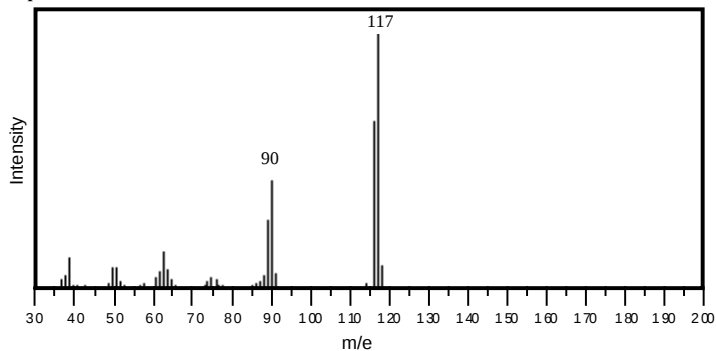
singlet, 171.0 ppm;
triplet, 78.8 ppm;
triplet, 70.2 ppm;
quartet, 53.6 ppm;
quartet, 17.3 ppm

Structure:

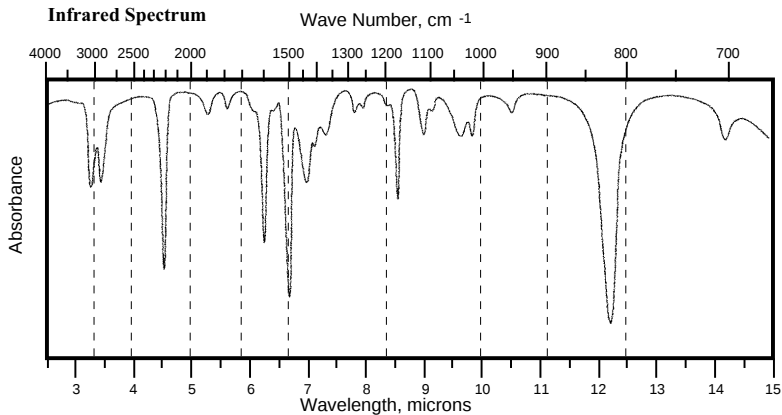
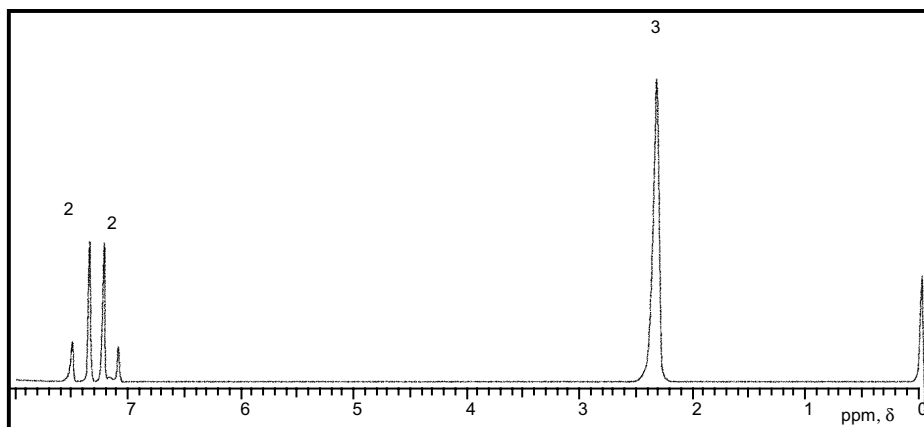


Compound 20 is a low-melting solid (melting point 30° C), that is insoluble in water. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 82.02; H, 6.02; N, 11.96.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

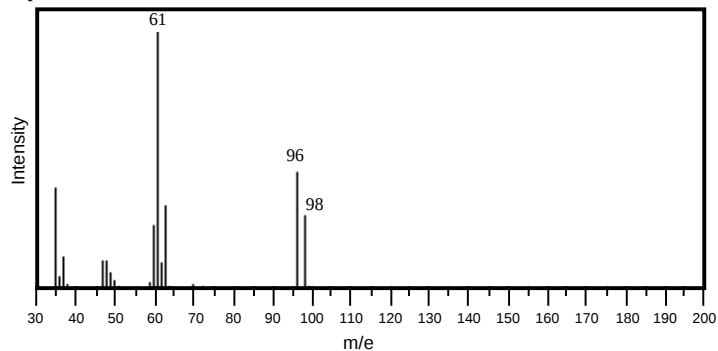
singlet, 142.0 ppm;
doublet, 131.9 ppm;
doublet, 129.9 ppm;
singlet, 116.5 ppm;
singlet, 109.5 ppm;
quartet, 22.0 ppm

Structure:

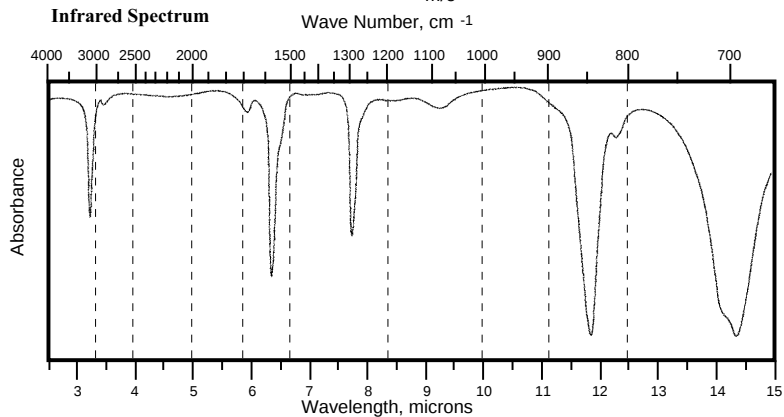
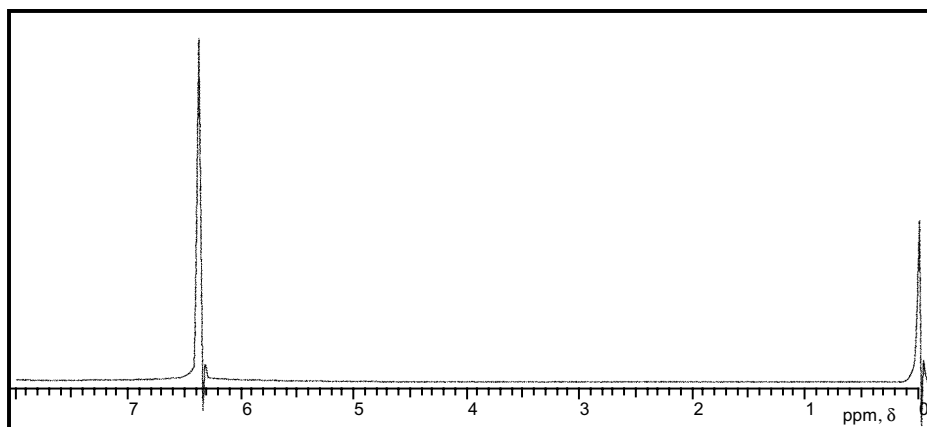


Compound 21 is a liquid (boiling point 60° C) that has **Z** stereochemistry. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 25.04; H, 1.05; contains two moles of a halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR

^{13}C Spectral Data:

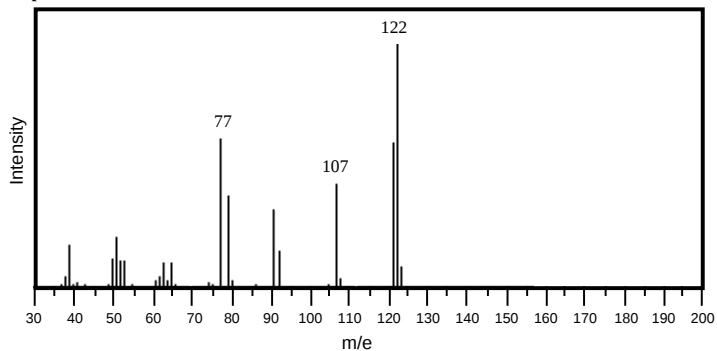
doublet, 116.3 ppm

Structure:

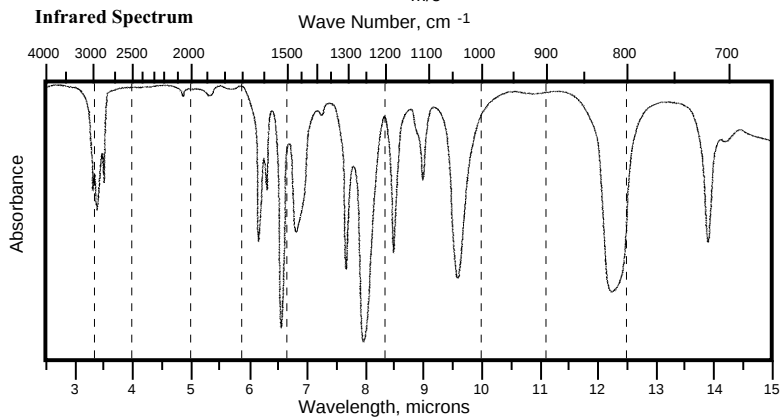
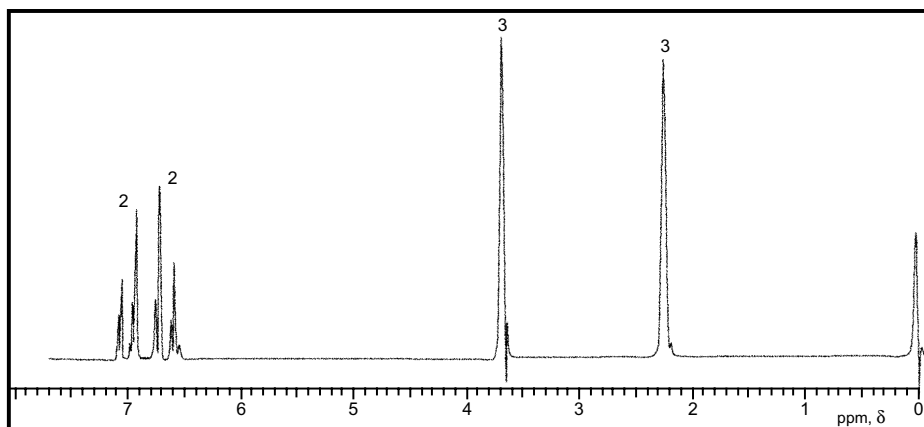


Compound 22 is a neutral, high-boiling liquid (boiling point 174 °C). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 78.65; H, 8.25; O, 13.10.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

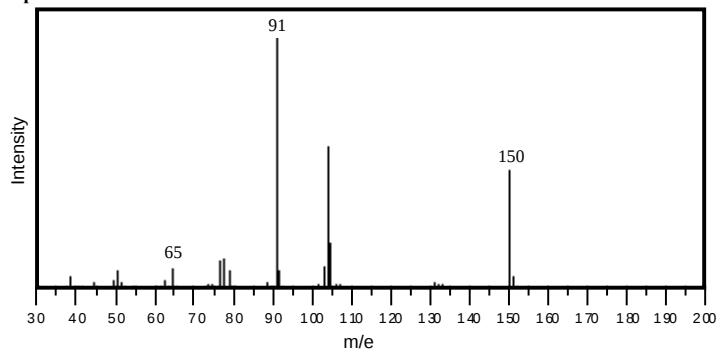
singlet, 159.0 ppm
 doublet, 130.2 ppm
 singlet, 130.0 ppm
 doublet, 114.0 ppm
 quartet, 56.0 ppm
 quartet, 22.0 ppm

Structure:

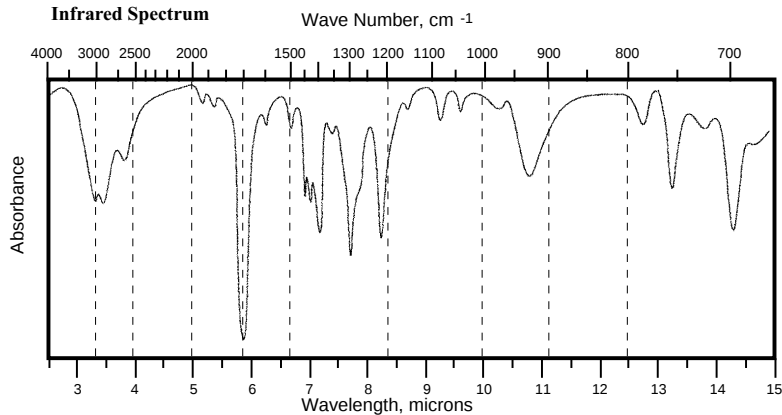
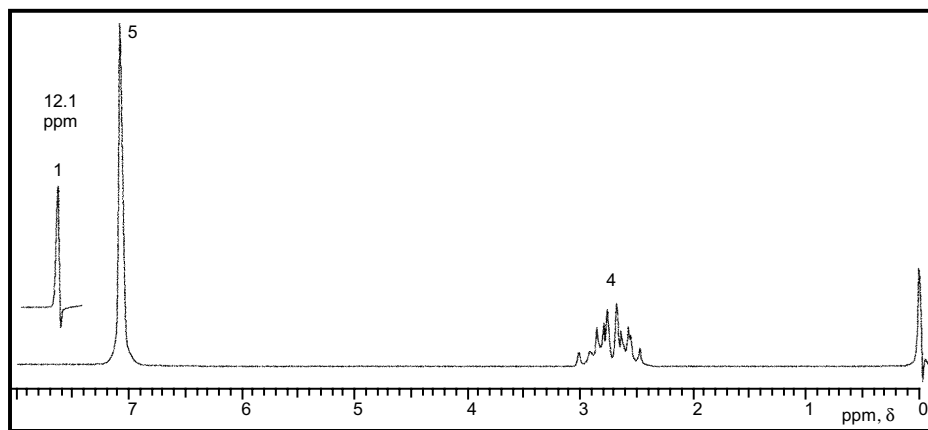


Compound 23 is a low-melting solid (melting point 49° C), that is slightly soluble in water, forming a weakly acidic solution. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 71.98; H, 6.71; O, 21.31

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

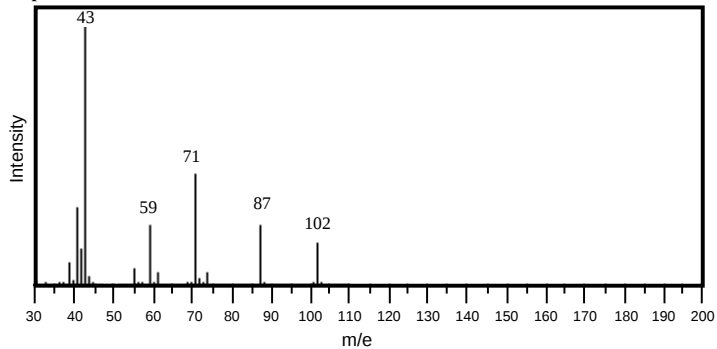
singlet, 177.0 ppm;
singlet, 138.8 ppm;
doublet, 128.6 ppm;
doublet, 128.3 ppm;
doublet, 125.8 ppm;
triplet, 41.3 ppm;
triplet, 36.5 ppm

Structure:

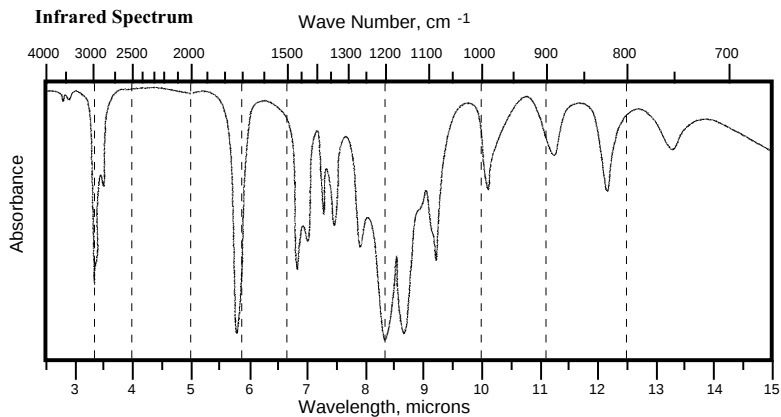
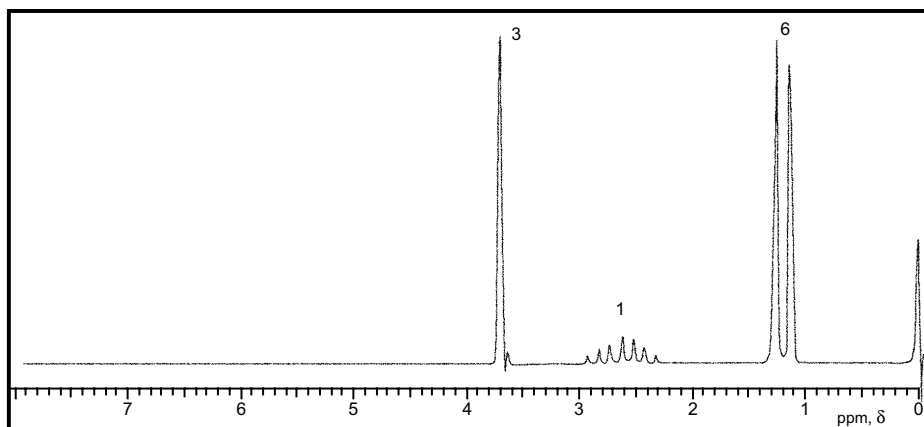


Compound 24 is a neutral, volatile liquid (boiling point 90 °C). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 58.80; H, 9.87; O, 31.33.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

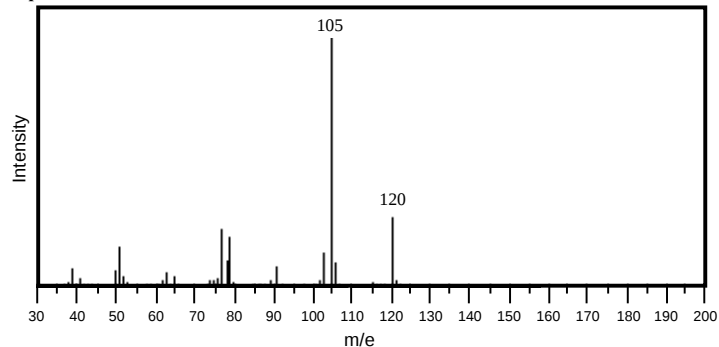
singlet, 174.5 ppm
 quartet, 50.7 ppm
 doublet, 35.2 ppm
 quartet, 18.5 ppm

Structure:

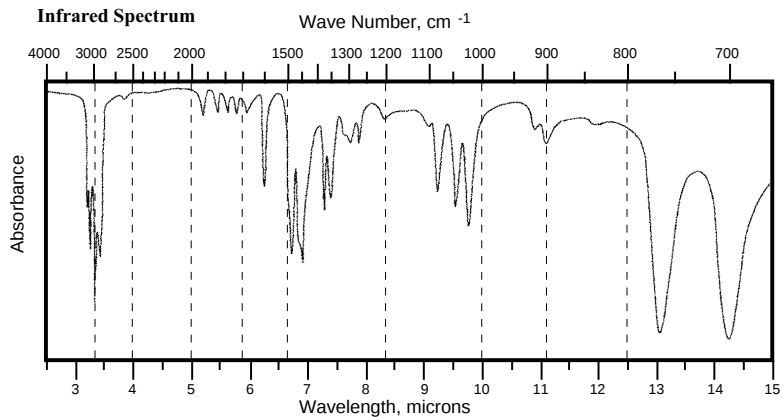
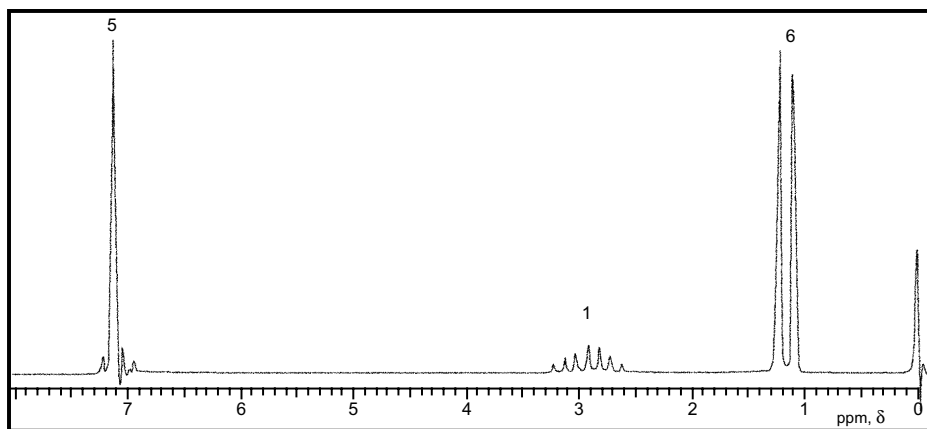


Compound 25 is a liquid (boiling point 151 °C), that is insoluble in water. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 89.94; H, 10.06.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

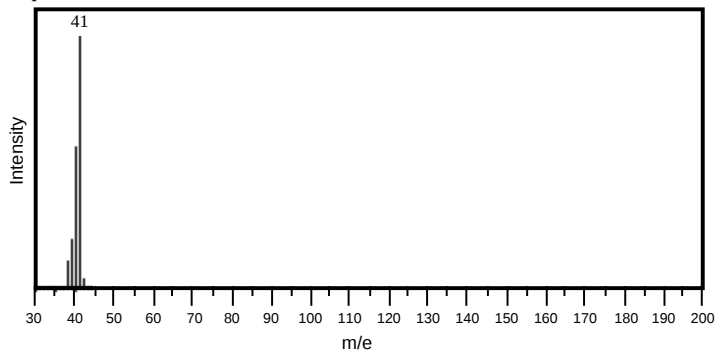
singlet, 148.7 ppm
 doublet, 128.2 ppm
 doublet, 126.3 ppm
 doublet, 125.7 ppm
 doublet, 40.2 ppm
 quartet, 25.5 ppm

Structure:

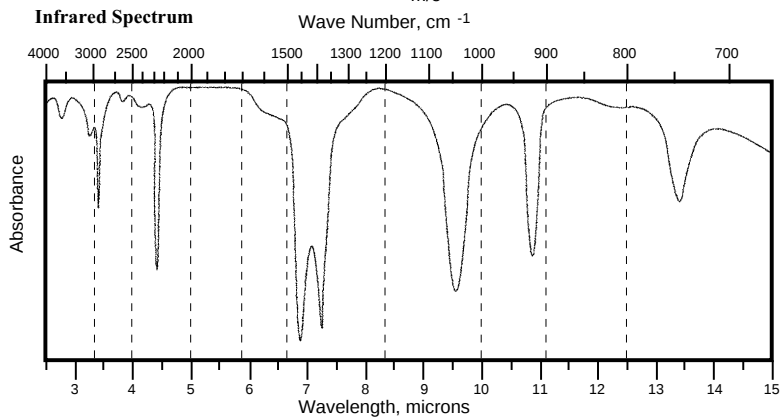
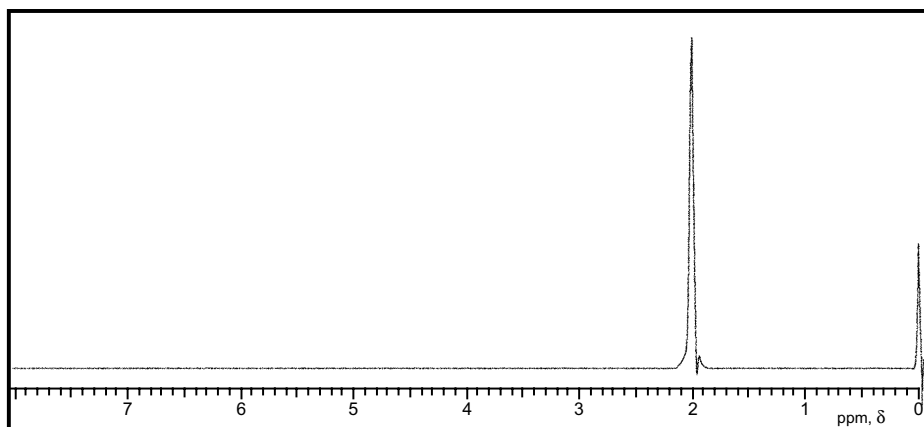


Compound 26 is a volatile liquid (boiling point 81.6 °C), that is used as a common organic solvent. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 58.51; H, 7.37; N, 34.12.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

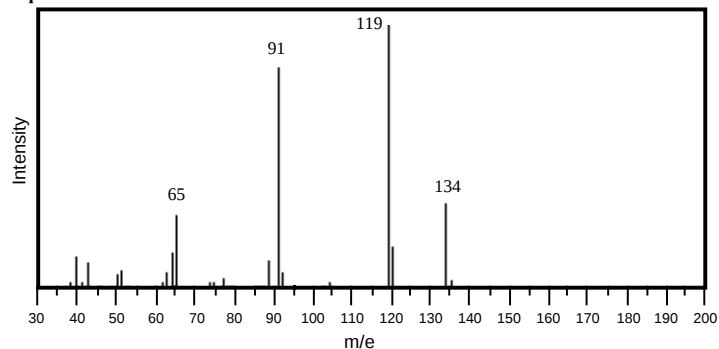
singlet, 114.9 ppm
quartet, 2.0 ppm

Structure:

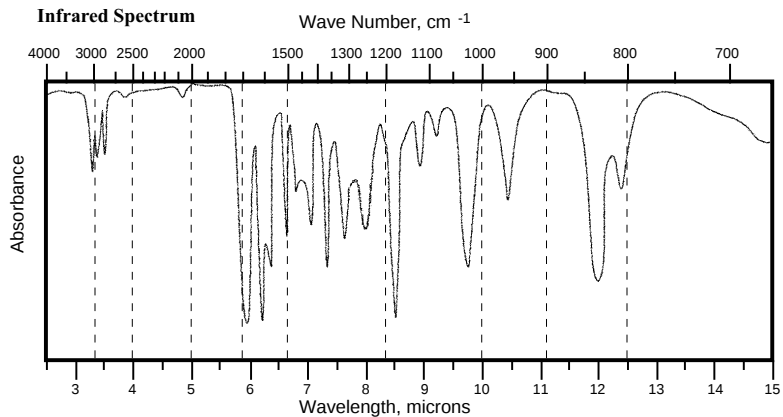
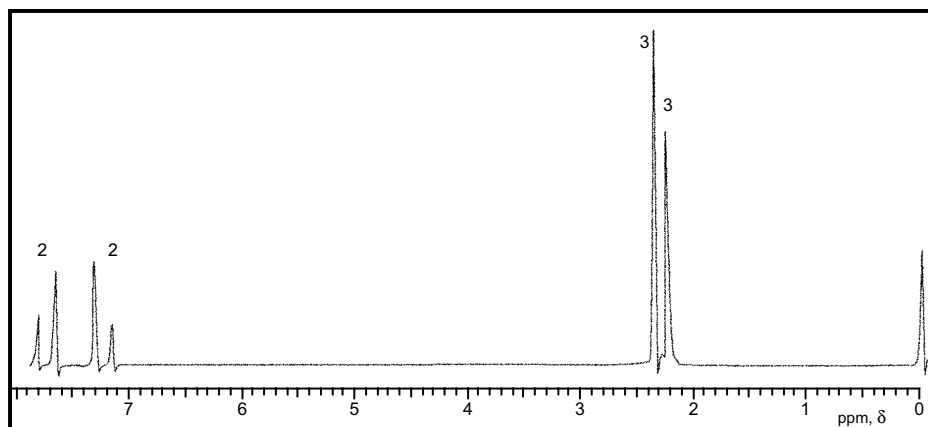


Compound 27 is a neutral, low-melting solid (melting point 22-24 °C). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 80.56; H, 7.51; O, 11.92.

Mass Spectrum



Infrared Spectrum

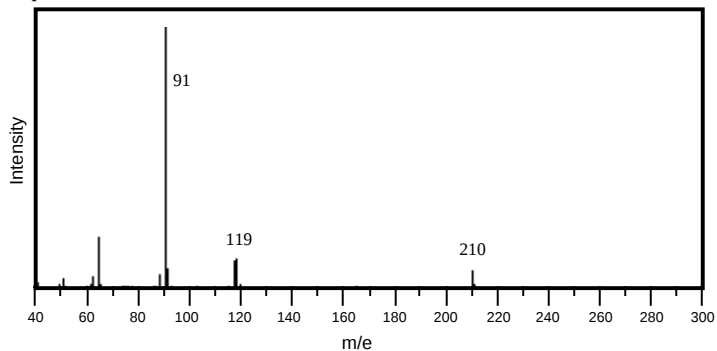
 ^1H NMR **^{13}C Spectral Data:**

singlet, 196.5 ppm
singlet, 142.1 ppm
singlet, 134.4 ppm
doublet, 129.1 ppm
doublet, 128.5 ppm
quartet, 22.8 ppm
quartet, 20.9 ppm

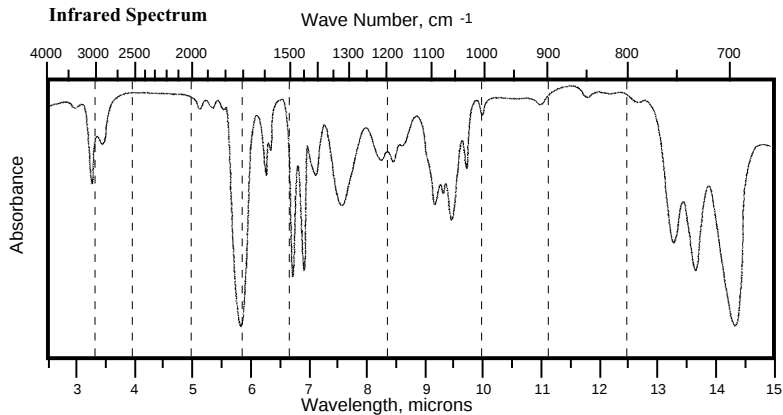
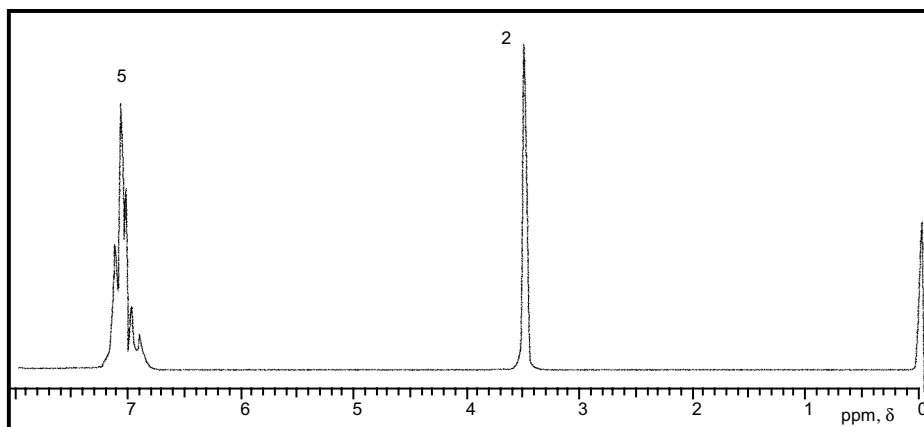
Structure:

Compound 28 is a neutral, low-melting solid (melting point 34° C). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 86.93; H, 5.35; O, 7.72.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

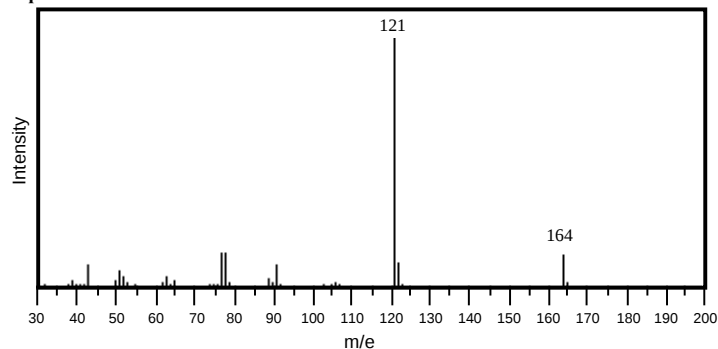
singlet, 208.2 ppm;
singlet, 139.4 ppm;
doublet, 128.3 ppm;
doublet, 128.2 ppm;
doublet, 125.7 ppm;
triplet, 48.7 ppm

Structure:

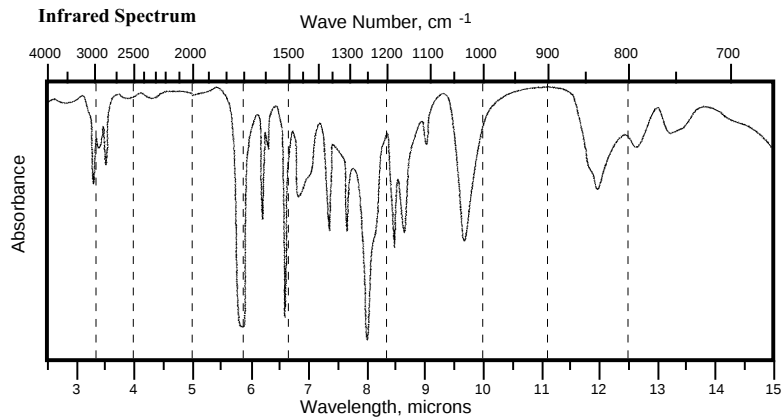
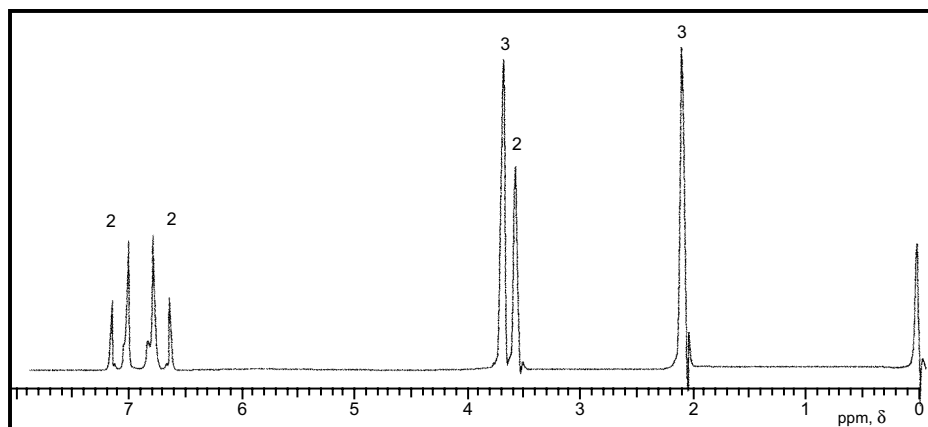


Compound 29 is a high-boiling, neutral liquid (boiling point 145 @ 25 mm²C). The Mass, IR, and ¹H NMR spectra, along with ¹³C NMR data, are given below. **Elemental Analysis:** C, 73.15; H, 7.37; O, 19.49.

Mass Spectrum



Infrared Spectrum

¹H NMR¹³C Spectral Data:

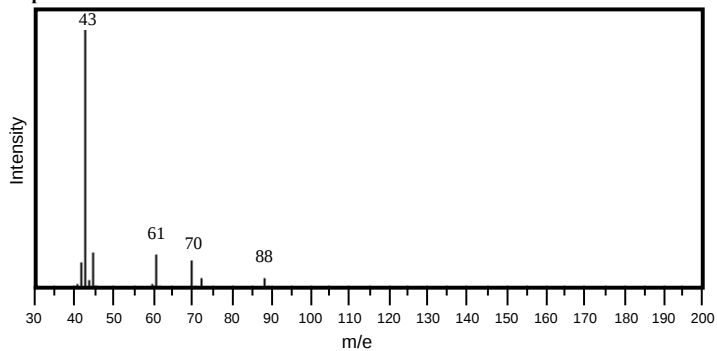
singlet, 207.1 ppm
singlet, 159.3 ppm
singlet, 131.1 ppm
doublet, 129.3 ppm
doublet, 114.2 ppm
quartet, 56.0 ppm
triplet, 51.3 ppm
quartet, 24.4 ppm

Structure:

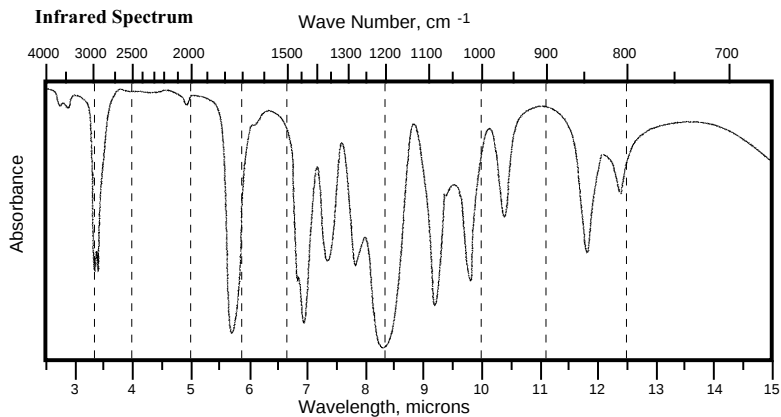
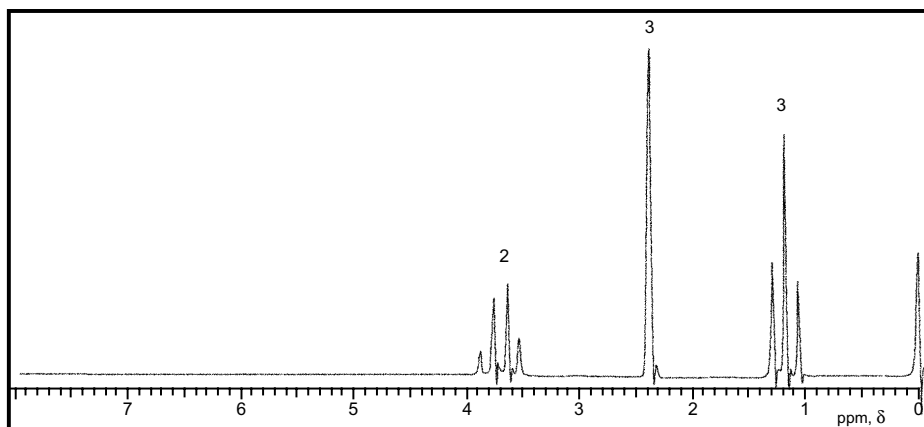


Compound 30 is a volatile liquid (boiling point 76 ° C), that is used as a common organic solvent. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 54.53; H, 9.15; O, 36.32.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

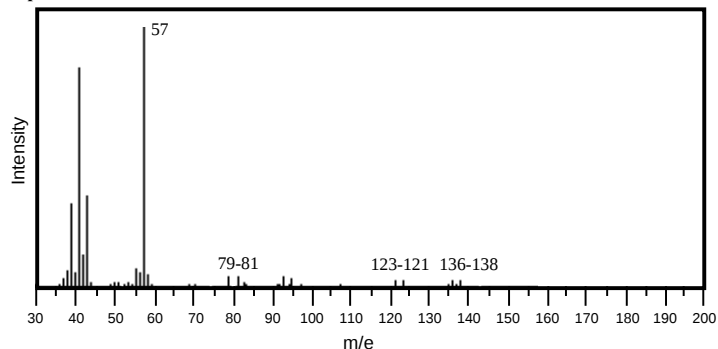
singlet, 171.0 ppm
triplet, 59.2 ppm
quartet, 17.3 ppm
quartet, 13.6 ppm

Structure:

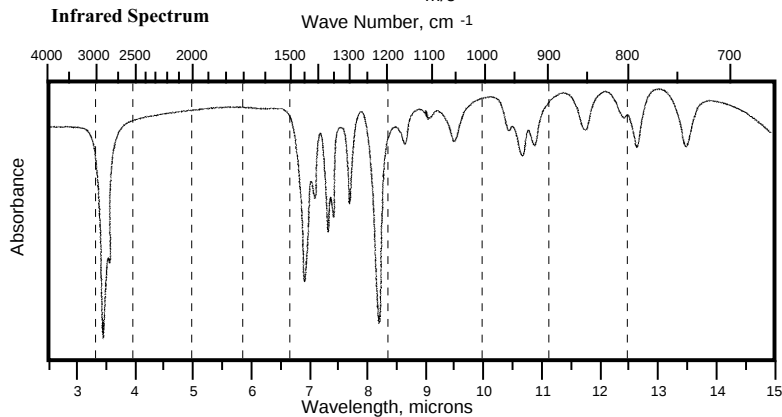
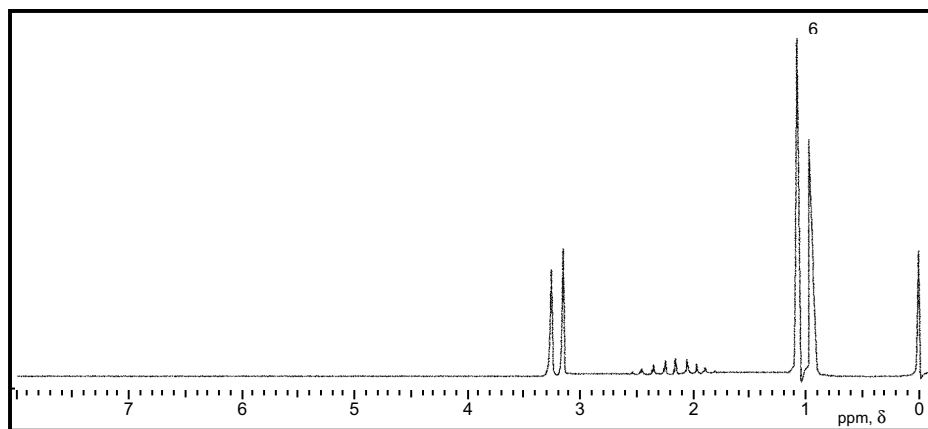


Compound 31 is a liquid (boiling point 122° C), that reacts with alkoxide to yield an ether. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below; the multiplet at 2.15 ppm consists of three overlapping septets. **Elemental Analysis:** C, 35.06; H, 6.62; contains halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

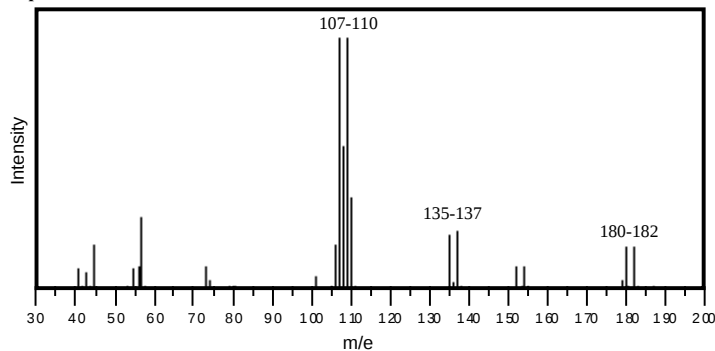
doublet, 32.3 ppm;
triplet, 42.0 ppm;
quartet, 20.7 ppm

Structure:

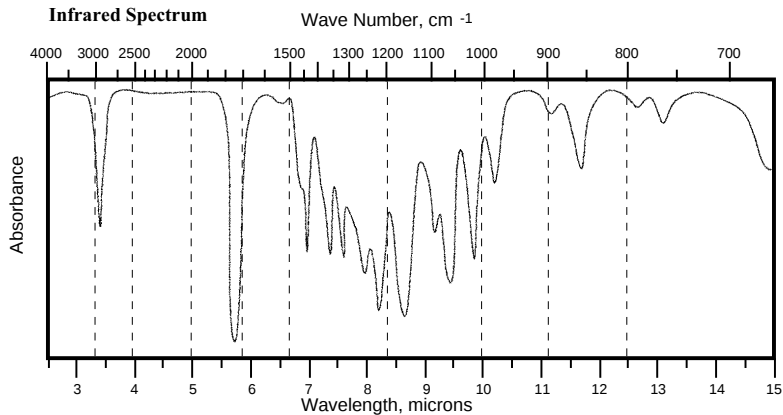
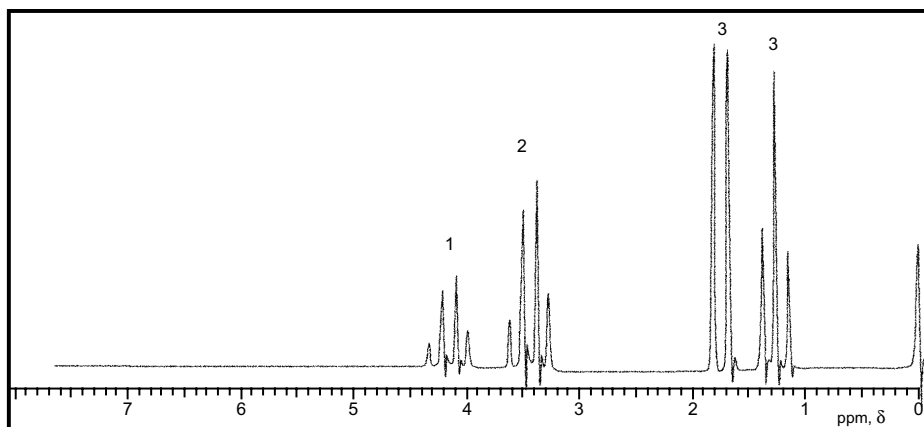


Compound 32 is a high-boiling neutral liquid that contains halogen. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 33.17; H, 5.01; O, 17.68; contains halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

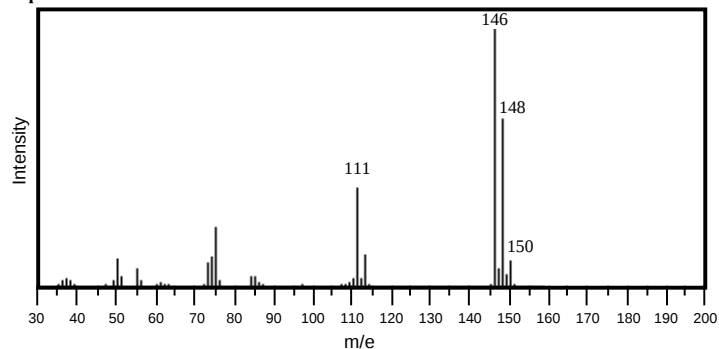
singlet, 172.0 ppm;
triplet, 59.5 ppm;
doublet, 57.7 ppm;
quartet, 20.4 ppm;
quartet, 13.6 ppm

Structure:

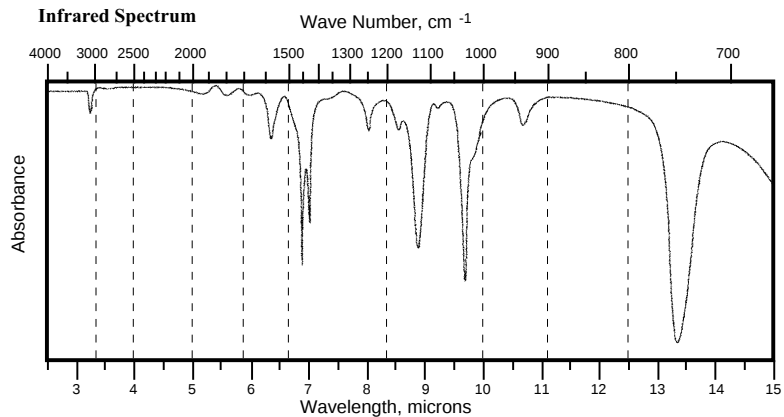
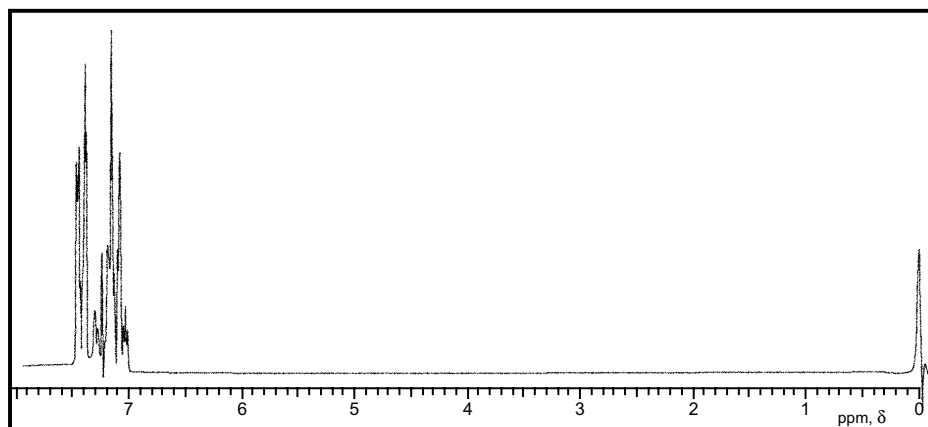


Compound 33 is a high-boiling, neutral liquid (boiling point 180 °C), that is insoluble in water. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 49.02; H, 2.74; contains two moles of a halogen.

Mass Spectrum



Infrared Spectrum

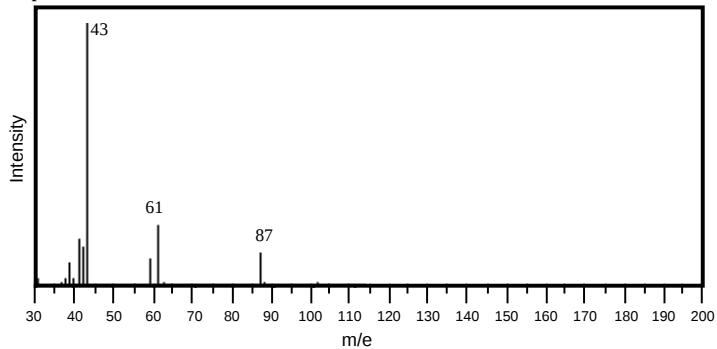
 ^1H NMR **^{13}C Spectral Data:**

singlet, 134.2 ppm
doublet, 130.3 ppm
doublet, 128.0 ppm

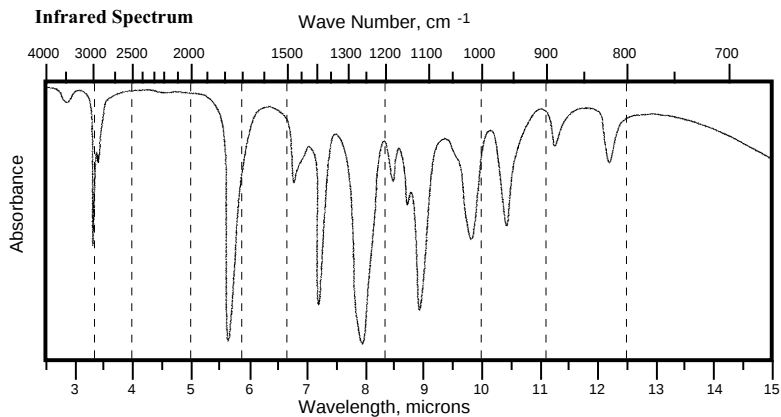
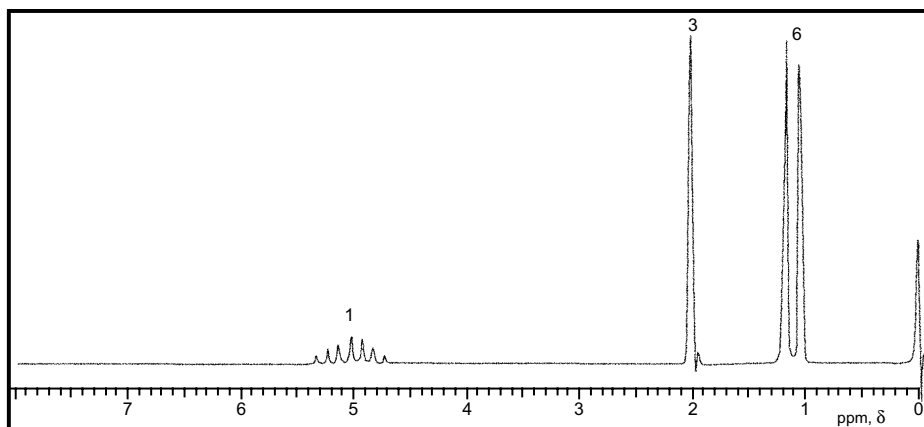
Structure:

Compound 34 is a volatile liquid (boiling point 88 °C). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below; the molecular ion ($m/e = 102$) does not show in the mass spectrum. **Elemental Analysis:** C, 58.80; H, 9.87; O, 31.33.

Mass Spectrum



Infrared Spectrum

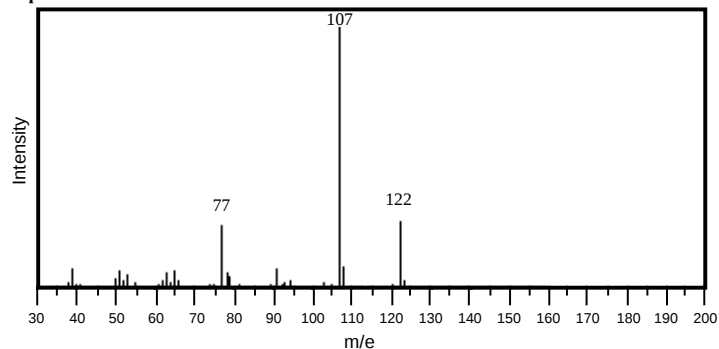
 ^1H NMR **^{13}C Spectral Data:**

singlet, 171.0 ppm
doublet, 68.3 ppm
quartet, 23.0 ppm
quartet, 17.6 ppm

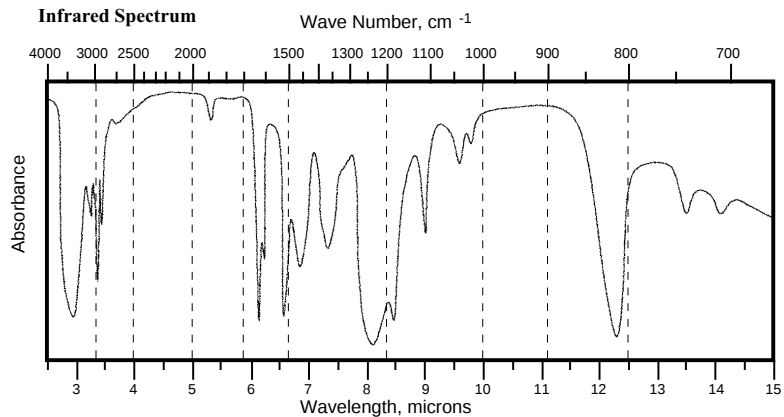
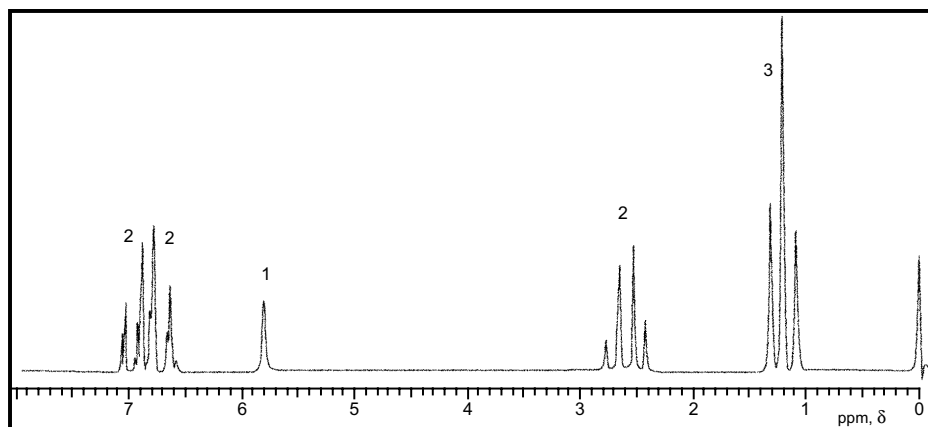
Structure:

Compound 35 is a low-melting solid (melting point 42-45 °C), that is slightly soluble in water, forming a weakly acidic solution. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 78.65; H, 8.25; O, 13.10.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

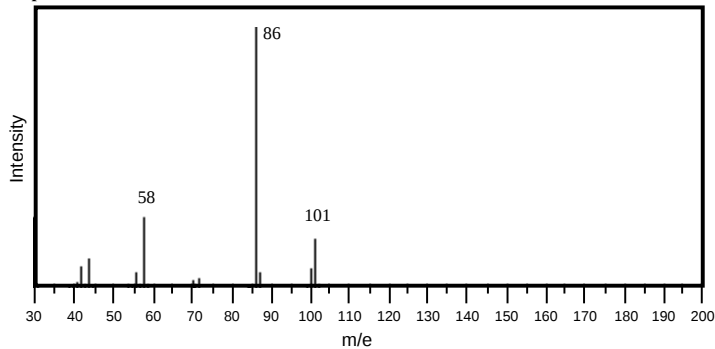
singlet, 154.5 ppm
singlet, 132.8 ppm
doublet, 129.3 ppm
doublet, 115.6 ppm
triplet, 31.1 ppm
quartet, 16.1 ppm

Structure:

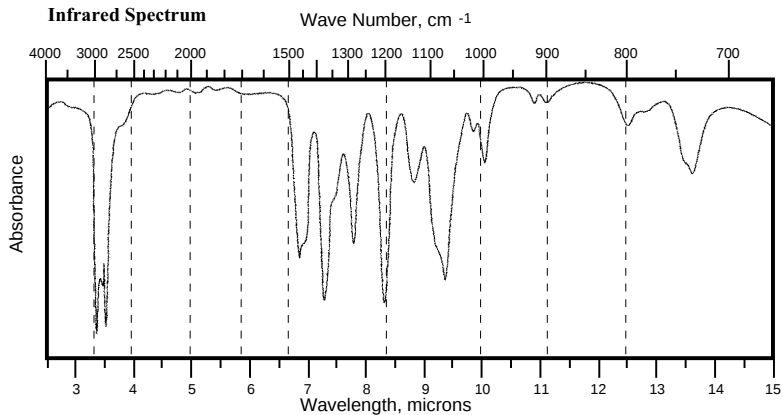
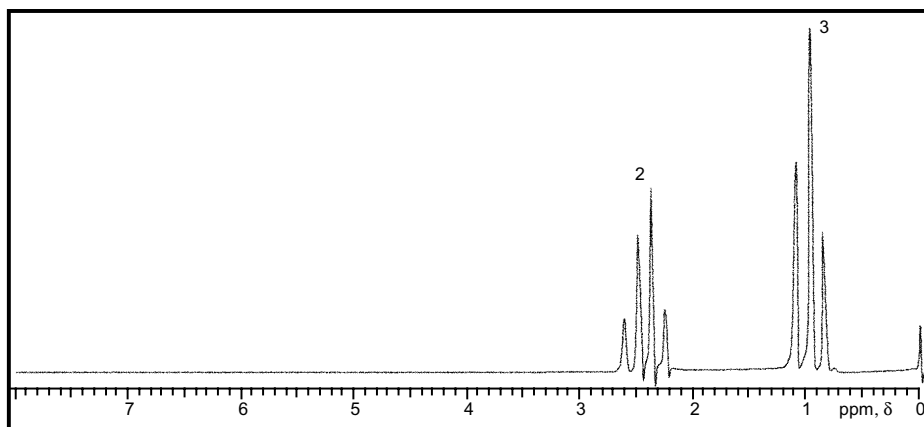


Compound 36 is a foul-smelling, basic liquid (boiling point 89° C). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 71.22; H, 14.94; N, 13.84

Mass Spectrum



Infrared Spectrum

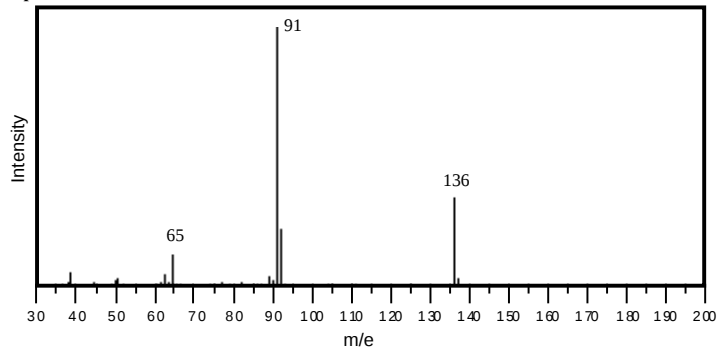
 ^1H NMR **^{13}C Spectral Data:**

triplet, 48.9 ppm;
quartet, 13.7 ppm

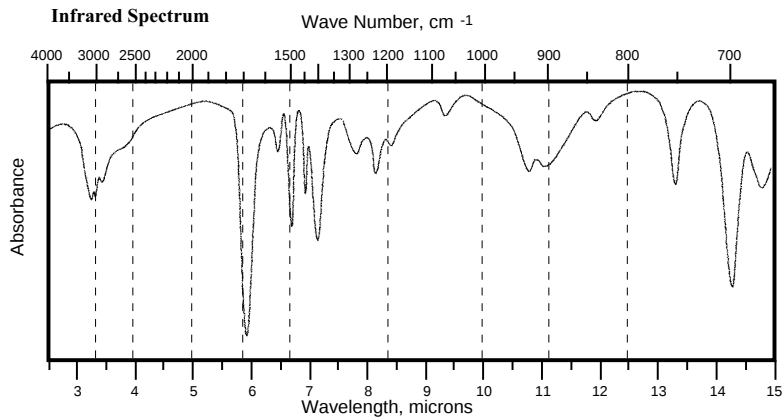
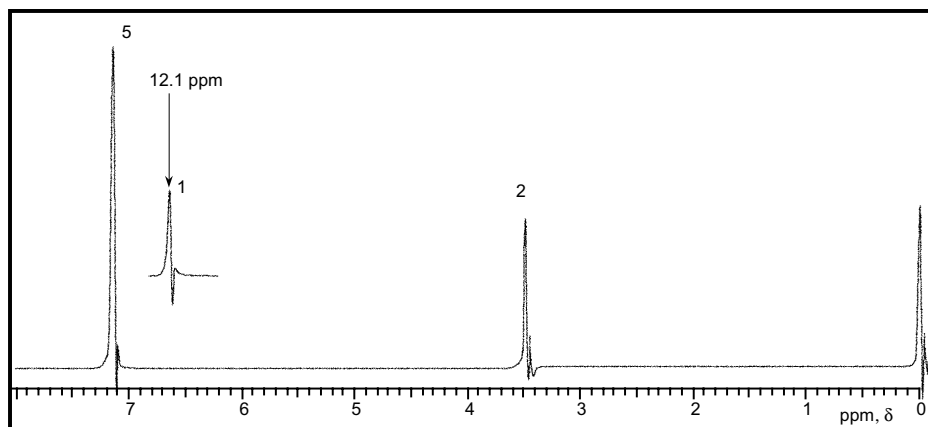
Structure:

Compound 37 is a solid (melting point 77° C), that is slightly soluble in water, forming an acidic solution. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. The broad band in the IR at 3400 - 2800 cm^{-1} is characteristic of this functional group. **Elemental Analysis:** C, 70.57; H, 5.92; O, 23.50.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

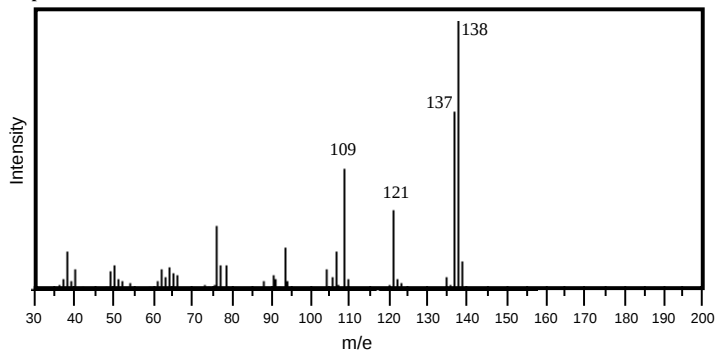
singlet, 178.0 ppm;
singlet, 135.0 ppm;
doublet, 129.9 ppm;
doublet, 128.9 ppm;
doublet, 127.3 ppm;
triplet, 43.8 ppm

Structure:

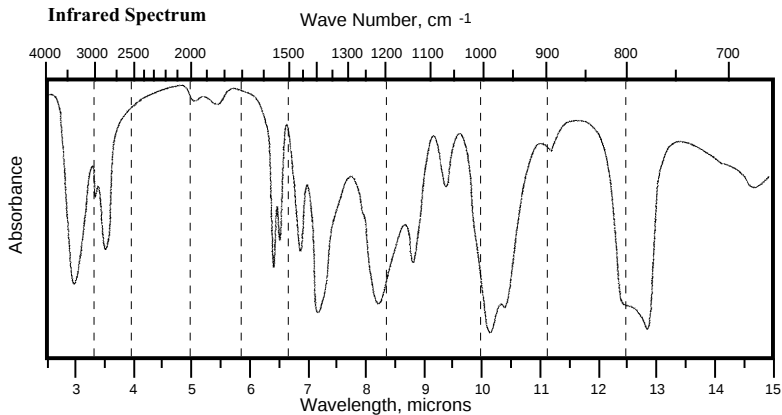
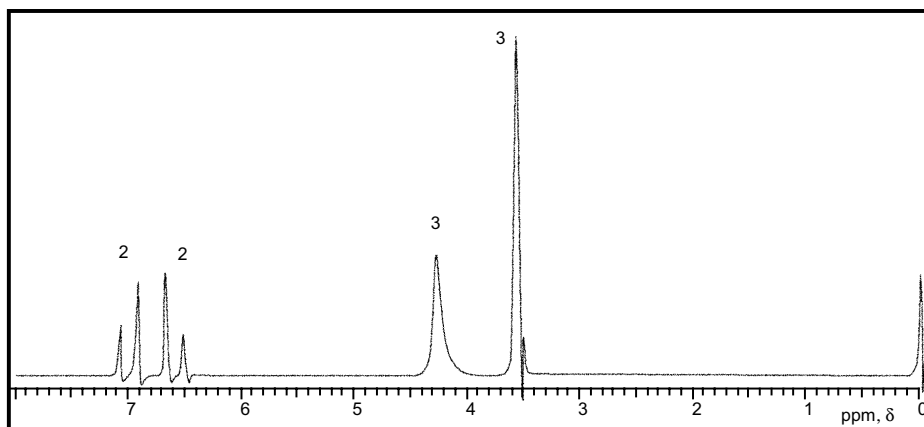


Compound 38 is a low-melting solid (melting point 25° C) which is very slightly soluble in water. The integration of the peak at 4.3 ppm in the ^1H NMR changes from 3 to 2 if the compound is exposed to D_2O . The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 69.54; H, 7.30; O, 23.16.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

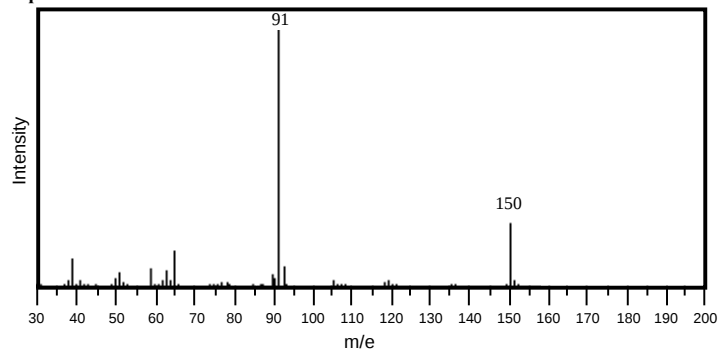
singlet, 160.9 ppm;
singlet, 133.2 ppm;
doublet, 128.3 ppm;
doublet, 114.3 ppm;
triplet, 71.0 ppm;
quartet, 56.0 ppm

Structure:

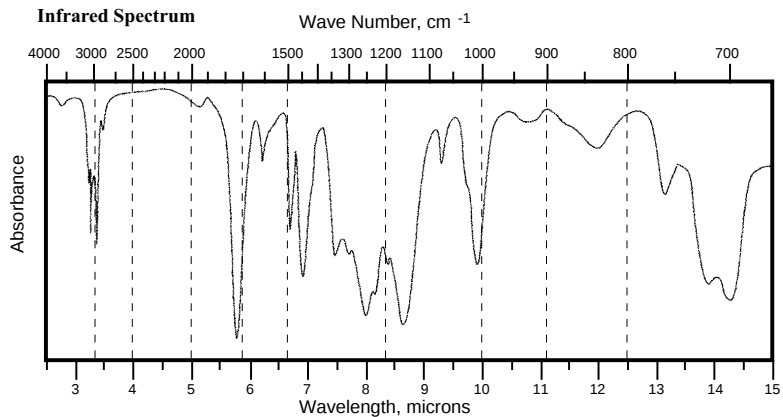
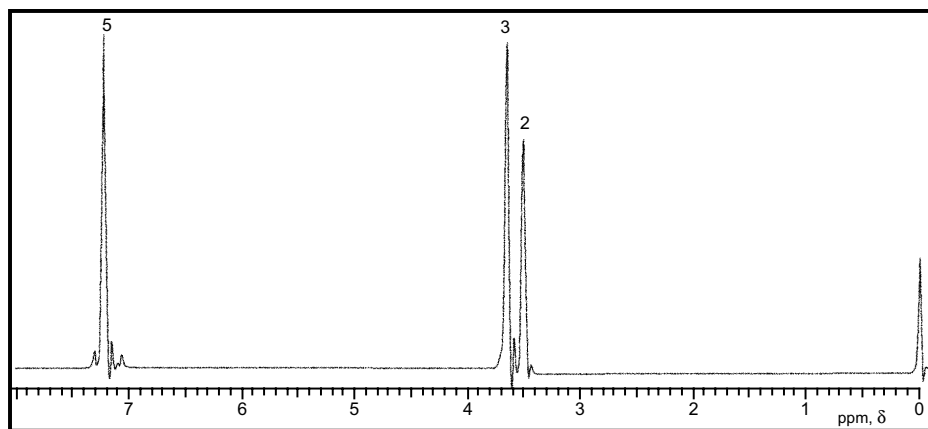


Compound 39 is a high-boiling, neutral liquid (boiling point 218 °C). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 71.98; H, 6.71; O, 21.31.

Mass Spectrum



Infrared Spectrum

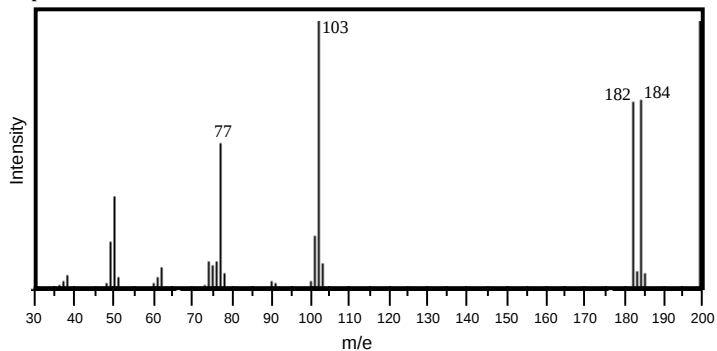
 ^1H NMR **^{13}C Spectral Data:**

singlet, 173.0 ppm
 singlet, 135.0 ppm
 doublet, 129.9 ppm
 doublet, 128.9 ppm
 doublet, 127.3 ppm
 quartet, 50.4 ppm
 triplet, 41.3 ppm

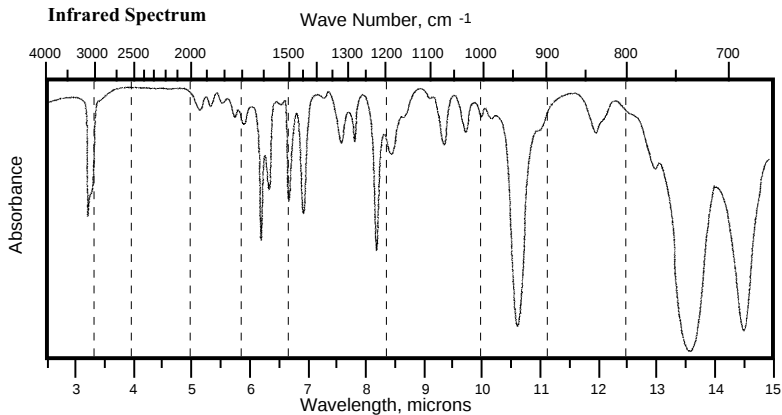
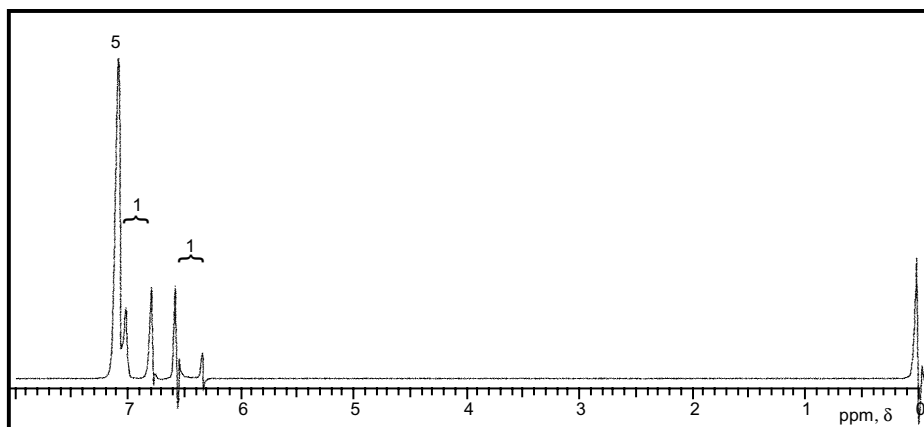
Structure:

Compound 40 is a high-boiling liquid that contains one mole of halogen. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. The coupling constant for the peaks at 6.45 and 6.9 ppm in the ^1H NMR is $J \approx 15$ Hz, suggesting **E** stereochemistry (**Z** stereochemistry typically displays a coupling constant of $J \approx 10$ Hz.) **Elemental Analysis:** C, 52.49; H, 3.85; contains halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

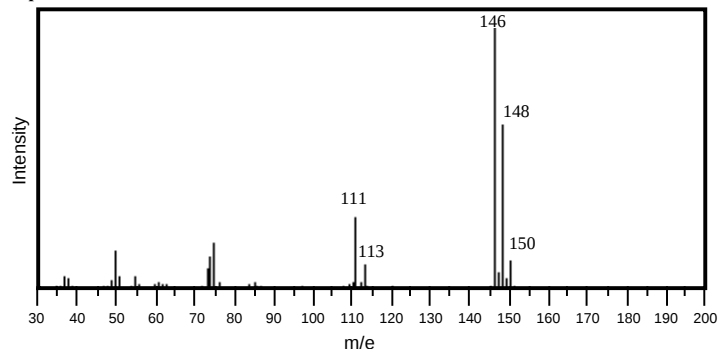
doublet, 150.0 ppm;
singlet, 134.9 ppm;
doublet, 128.4 ppm;
doublet, 127.7 ppm;
doublet, 126.2 ppm;
doublet, 98.2 ppm

Structure:

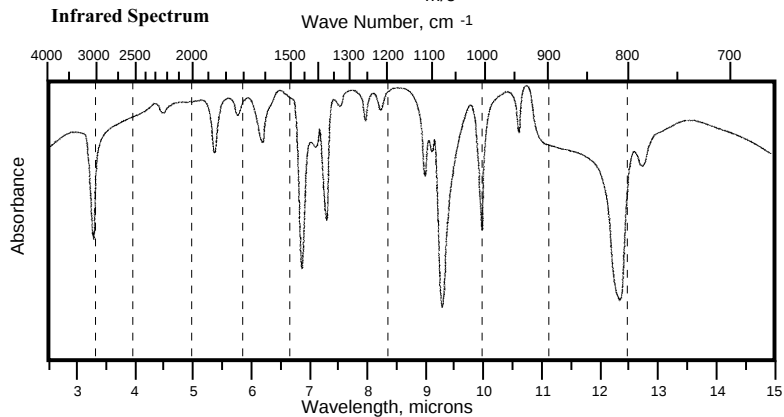
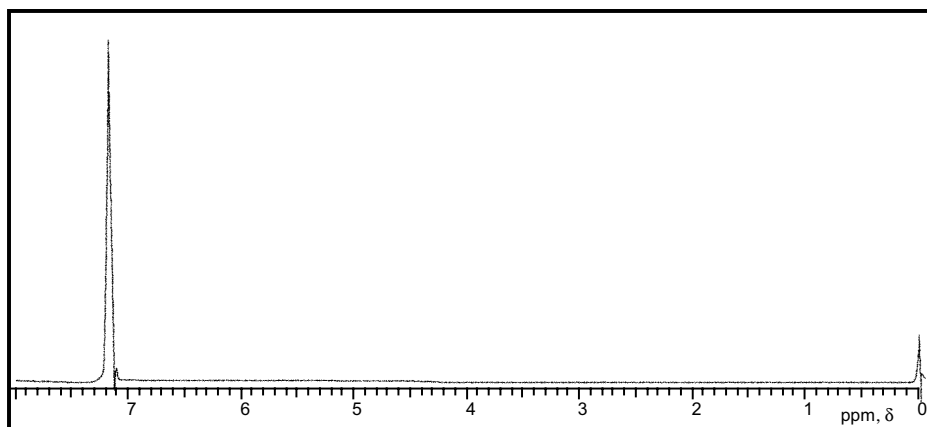


Compound 41 is a volatile solid (melting point 53°C) containing two moles of a halogen. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 49.02; H, 2.74; contains two moles of a halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

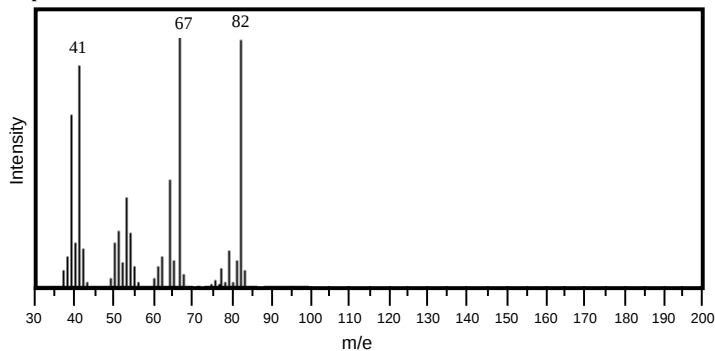
singlet, 136.7 ppm;
doublet, 115.9 ppm

Structure:

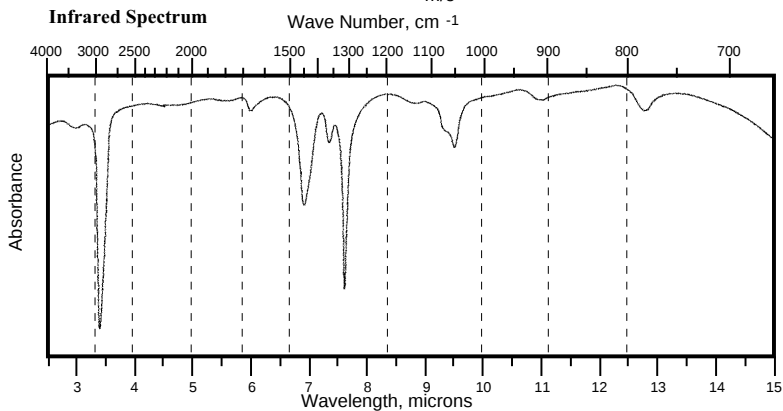
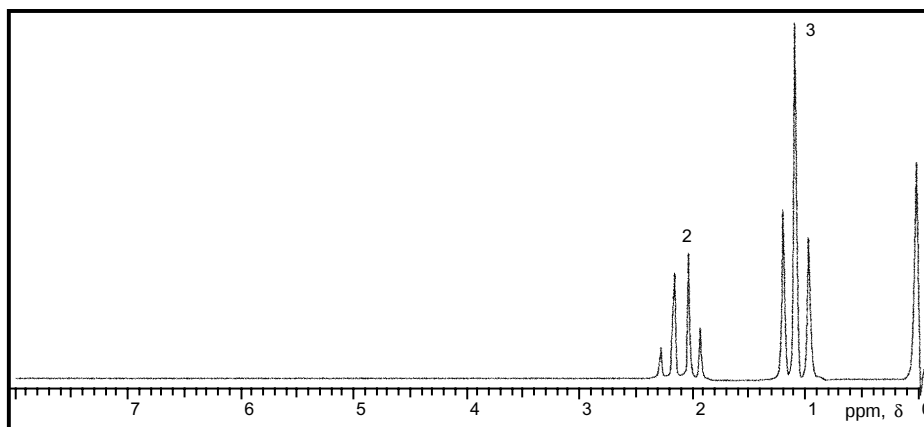


Compound 42 is a liquid (boiling point 81°C), which reacts with bromine in CCl_4 to yield a 1,1,2,2-tetrabromide. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. The stretching vibration for the functional group does not appear in the IR because of symmetry. **Elemental Analysis:** C, 87.73; H, 12.27

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

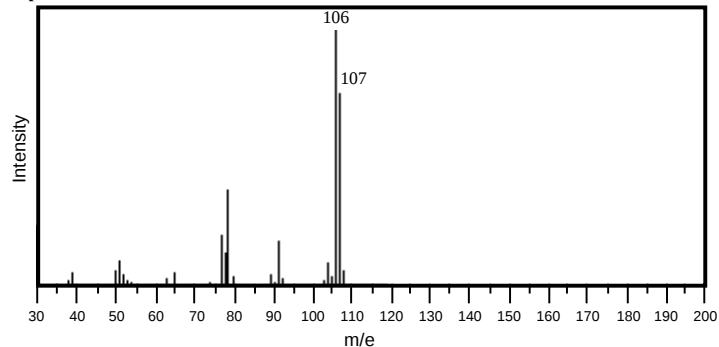
singlet, 80.7 ppm;
quartet, 12.7 ppm;
triplet, 10.6 ppm

Structure:

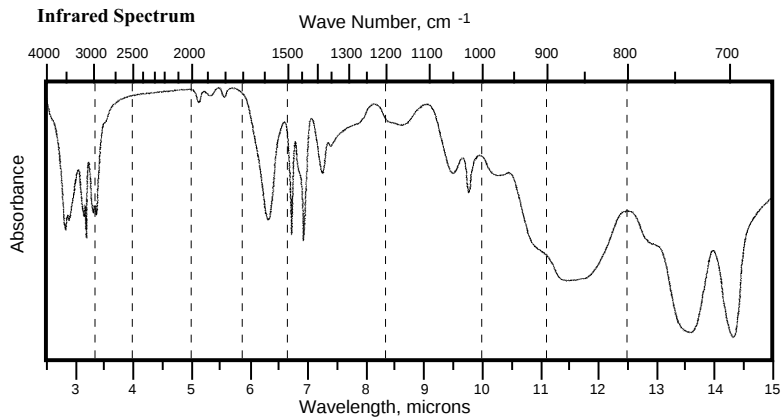
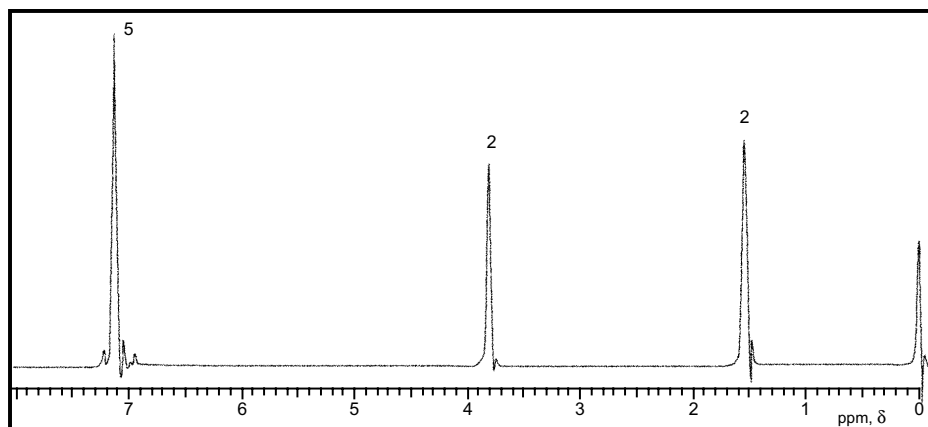


Compound 43 is a basic liquid (boiling point 71 °C @ 10 mm Hg). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 78.46; H, 8.47; N, 13.07.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

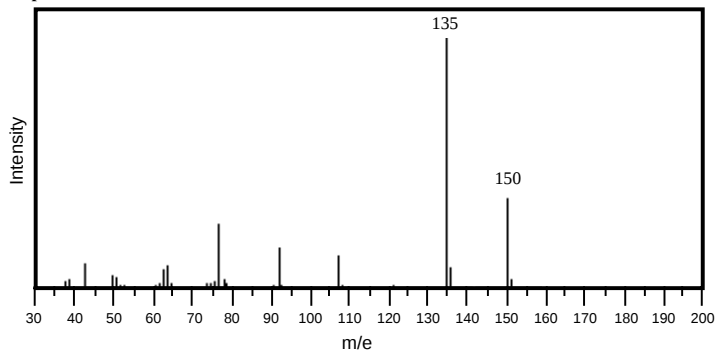
singlet, 142.4 ppm
 doublet, 128.3 ppm
 doublet, 127.1 ppm
 doublet, 126.5 ppm
 triplet, 50.3 ppm

Structure:

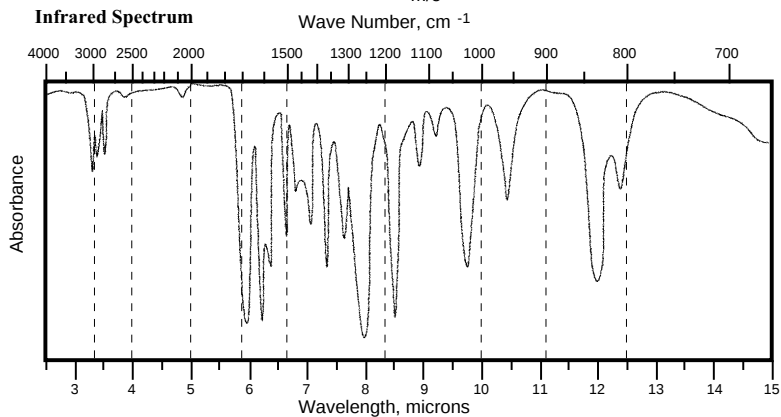
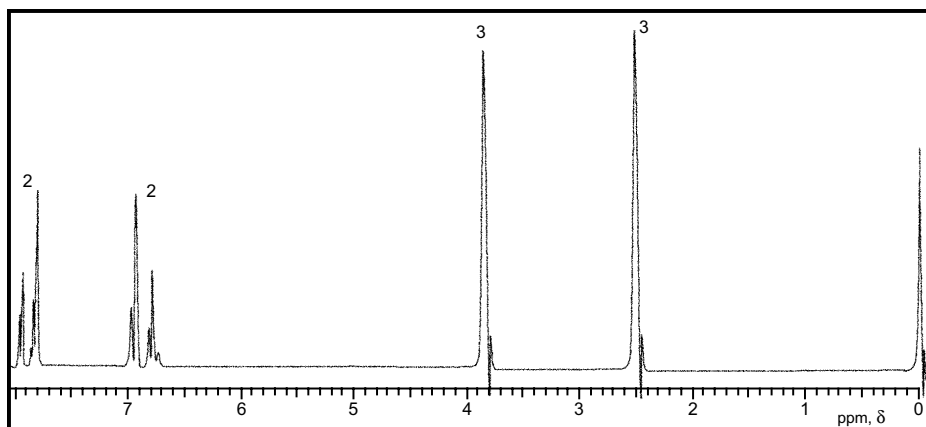


Compound 44 is a low-melting solid (melting point 36-38 °C). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 71.98; H, 6.71; O, 21.31.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

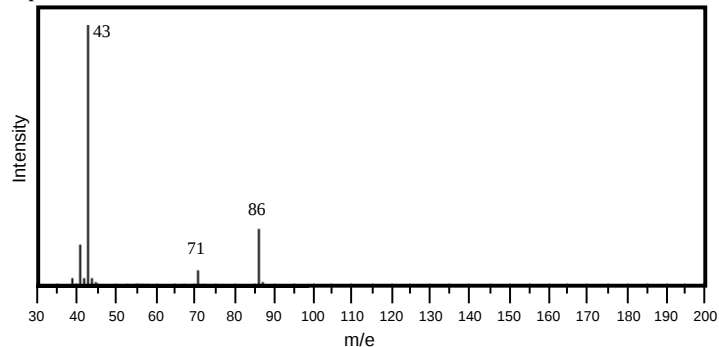
singlet, 196.5 ppm
 singlet, 166.4 ppm
 singlet, 129.7 ppm
 doublet, 129.6 ppm
 doublet, 114.0 ppm
 quartet, 56.0 ppm
 quartet, 27.0 ppm

Structure:

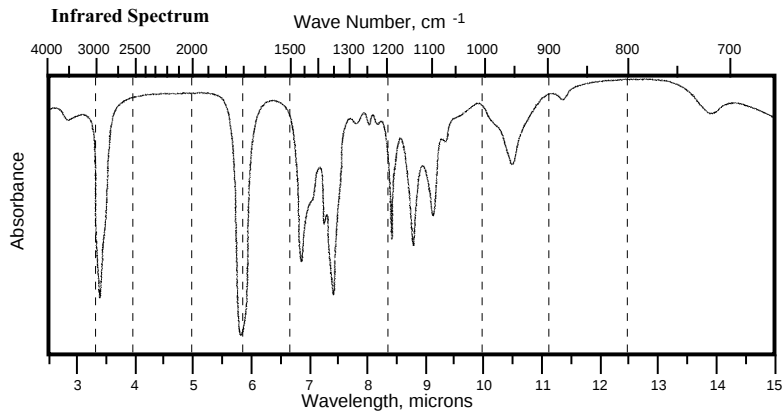
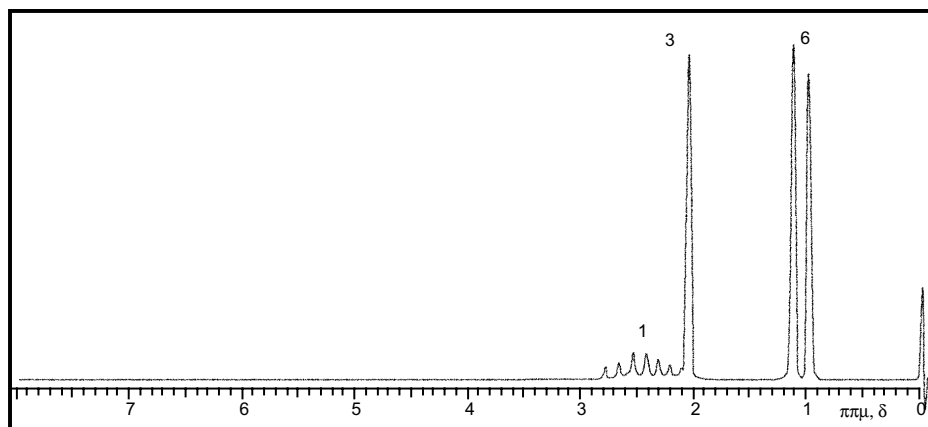


Compound 45 is a liquid (boiling point 94° C) that can be prepared by the oxidation of a secondary alcohol. The compound reacts with I_2 in aqueous base to give a yellow precipitate of CHI_3 (the iodoform test). The Mass, IR, and 1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 69.72; H, 11.70; O, 18.58

Mass Spectrum



Infrared Spectrum

 1H NMR ^{13}C Spectral Data:

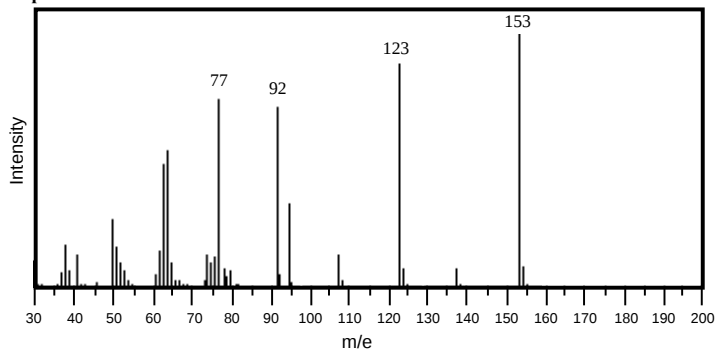
singlet, 210.2 ppm;
doublet, 45.2 ppm;
quartet, 22.2 ppm;
quartet, 16.7 ppm

Structure:

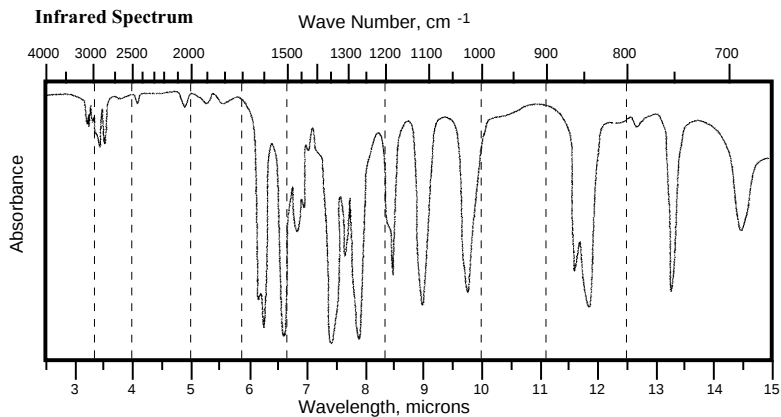
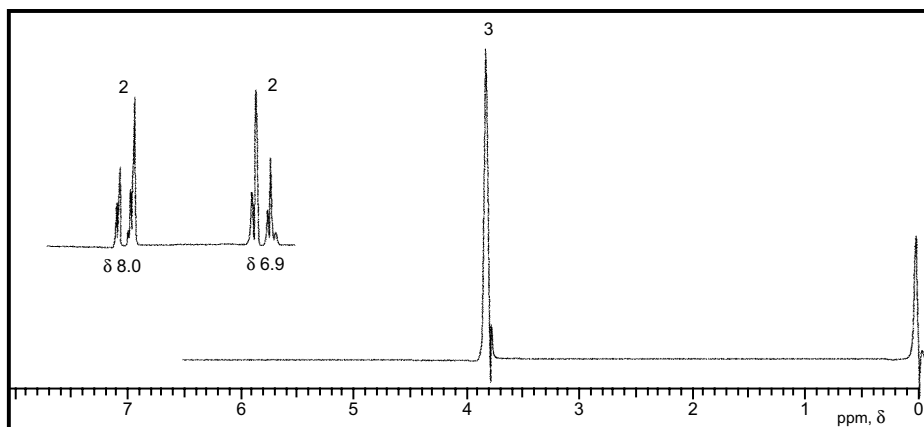


Compound is a neutral, low-melting solid (melting point 50-52 °C). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 54.90; H, 4.61; N, 9.15; O, 31.34.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

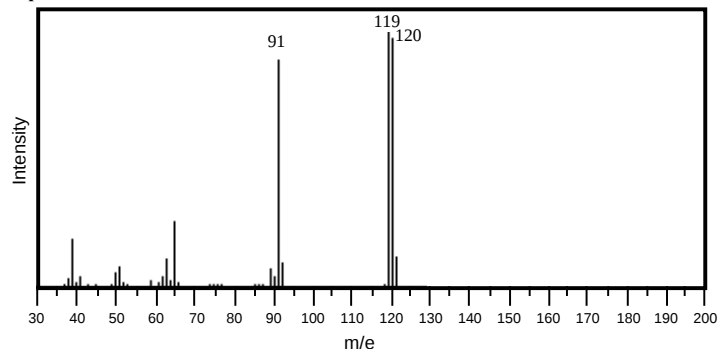
singlet, 168.1 ppm
singlet, 140.7 ppm
doublet, 124.6 ppm
doublet, 115.0 ppm
quartet, 56.0 ppm

Structure:

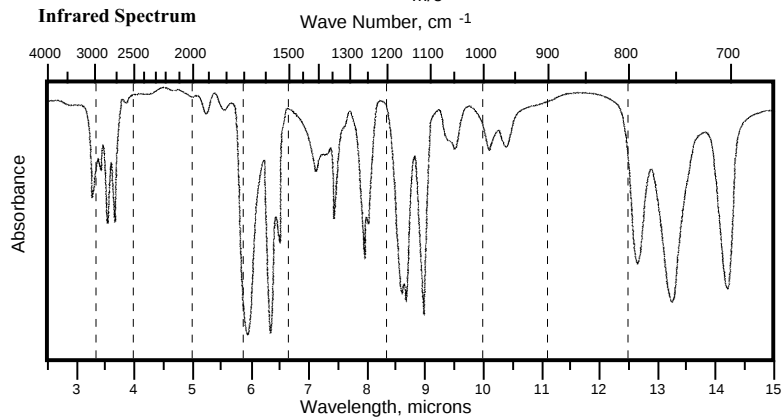
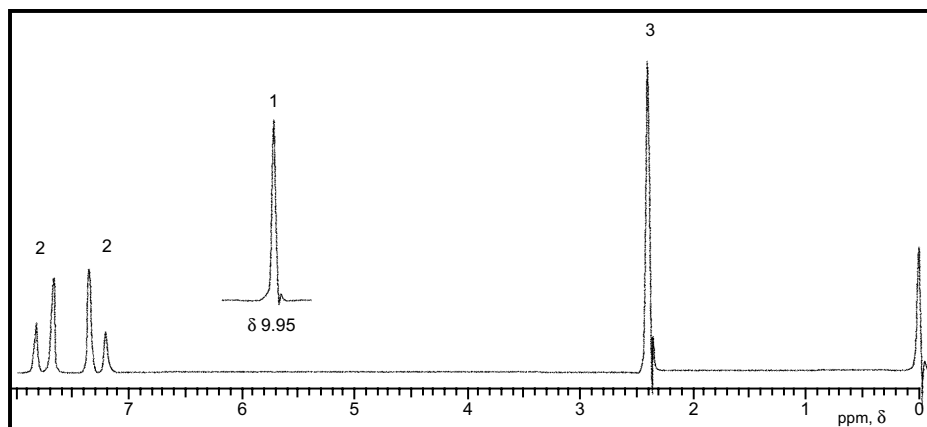


Compound 47 is a high-boiling liquid (boiling point 204-205 °C), that reacts with Ag^+ ion in aqueous ammonia to form a “silver mirror” (the Tollens test). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 79.97; H, 6.71; O, 13.32.

Mass Spectrum



Infrared Spectrum

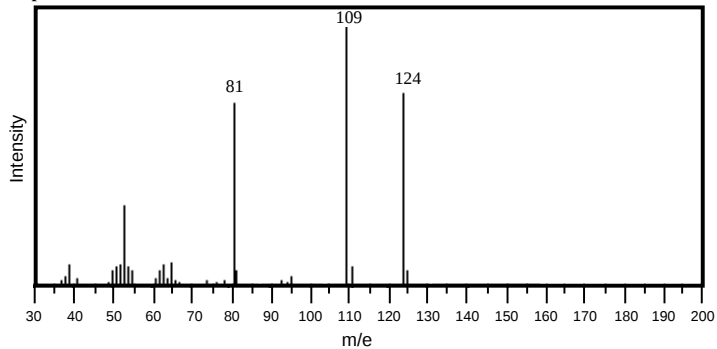
 ^1H NMR **^{13}C Spectral Data:**

singlet, 190.0 ppm
singlet, 143.5 ppm
singlet, 133.7 ppm
doublet, 129.7 ppm
doublet, 129.6 ppm
quartet, 22.0 ppm

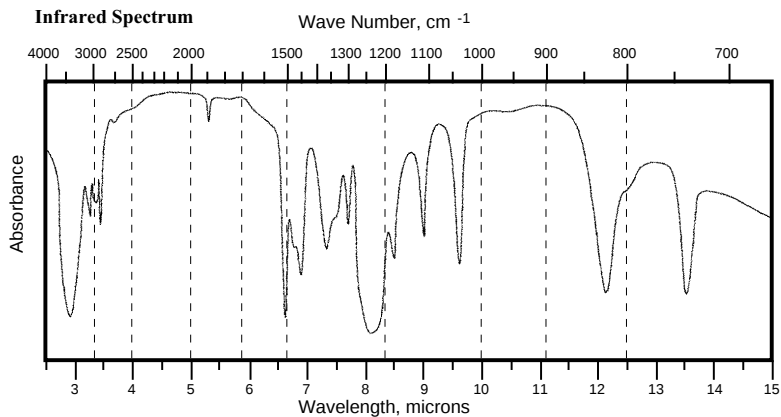
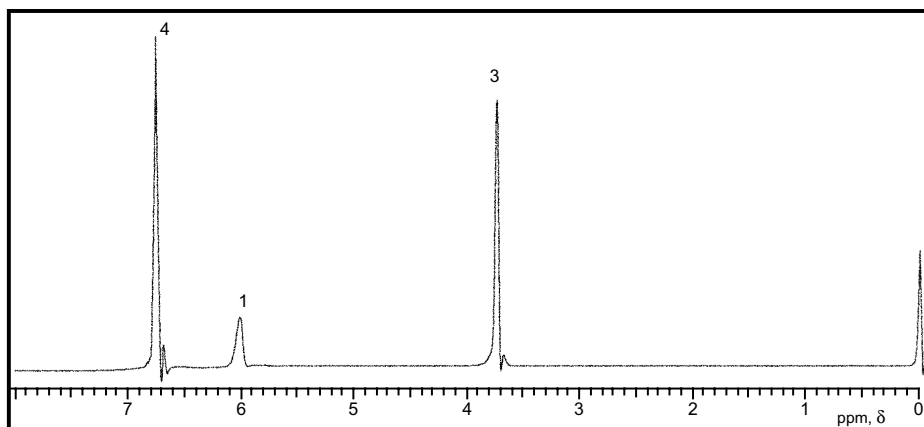
Structure:

Compound 48 is a low-melting solid (melting point 55-57 °C), that is soluble in dilute aqueous base, but precipitates on acidification. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 67.73; H, 6.50; O, 25.78.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

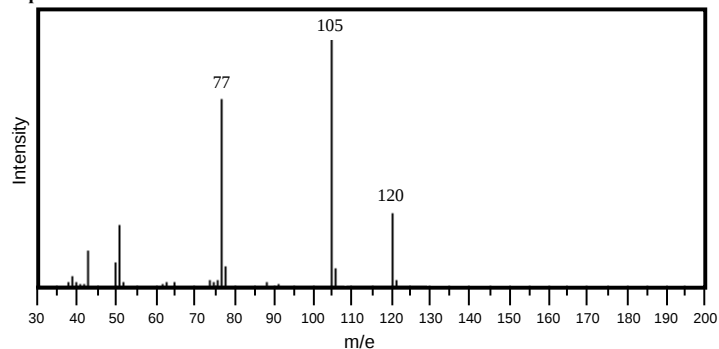
singlet, 154.6 ppm
singlet, 149.6 ppm
doublet, 116.7 ppm
doublet, 115.5 ppm
quartet, 56.0 ppm

Structure:

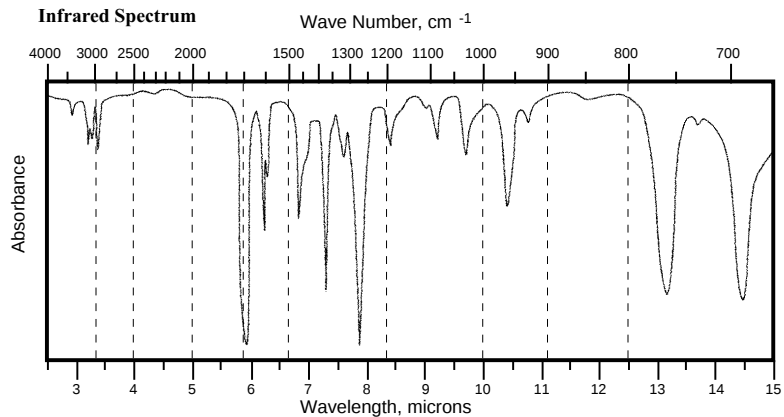
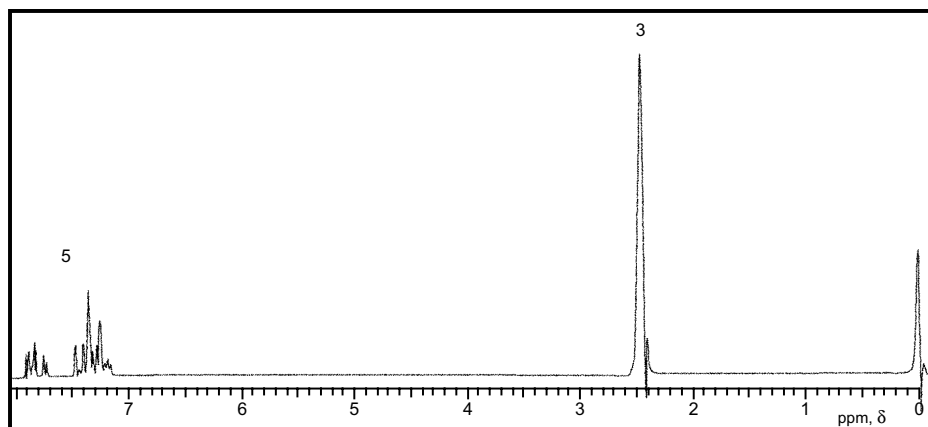


Compound 49 is a low-melting solid (melting point 19-20 °C), that reacts with I_2 in aqueous base to give a yellow precipitate of CHI_3 (the iodoform test). The Mass, IR, and 1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 79.97; H, 6.71; O, 13.32.

Mass Spectrum



Infrared Spectrum

 1H NMR ^{13}C Spectral Data:

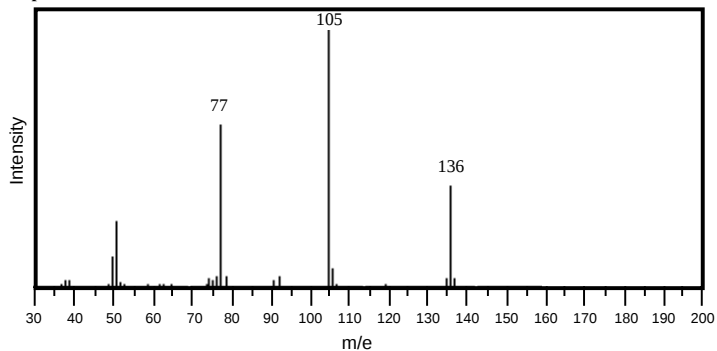
singlet, 196.5 ppm
singlet, 137.4 ppm
doublet, 132.9 ppm
doublet, 128.6 ppm
doublet, 128.4 ppm
quartet, 27.0 ppm

Structure:

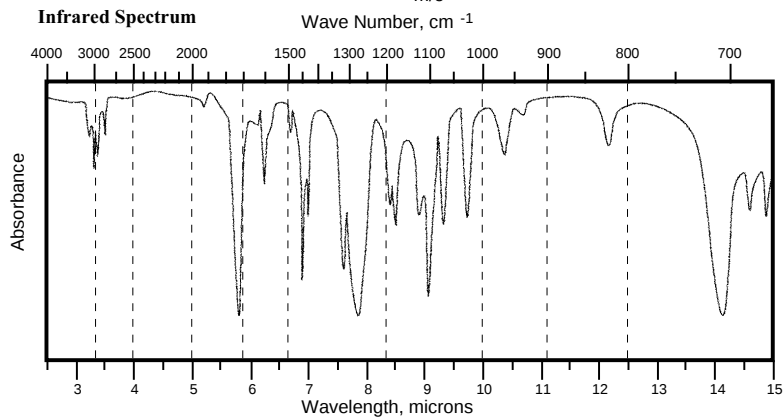
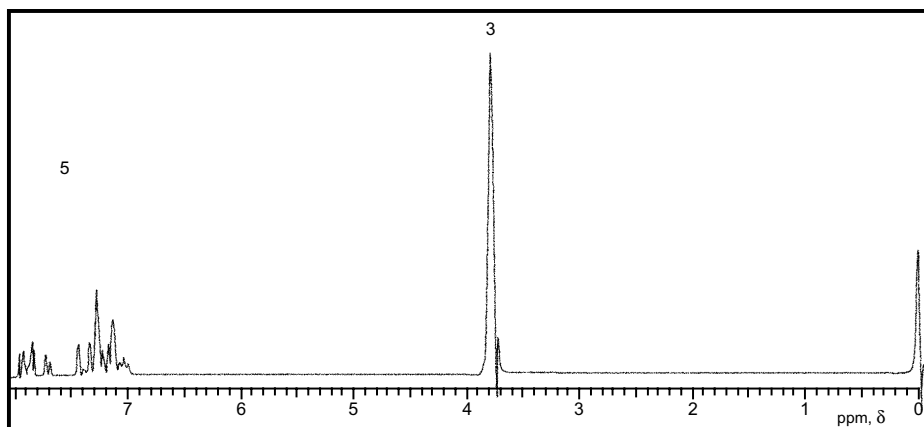


Compound 50 is a neutral, high-boiling liquid (boiling point 198-199 °C). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 70.57; H, 5.92; O, 23.50.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

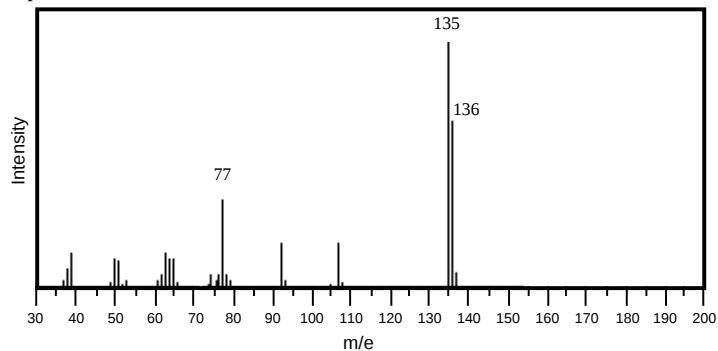
singlet, 167.0 ppm
 doublet, 132.8 ppm
 singlet, 130.5 ppm
 doublet, 129.7 ppm
 doublet, 128.4 ppm
 quartet, 50.0 ppm

Structure:

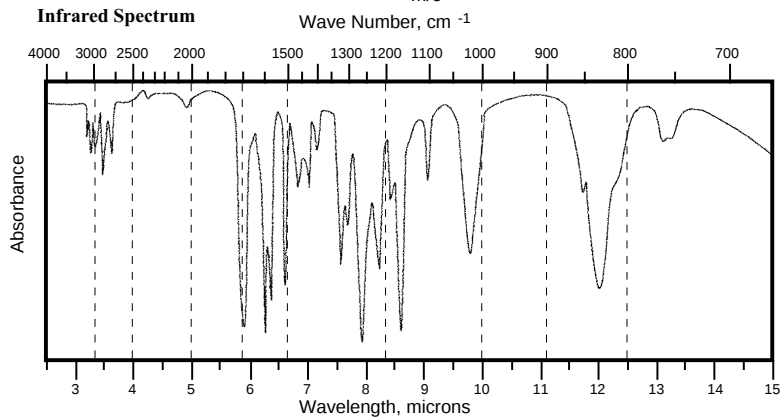
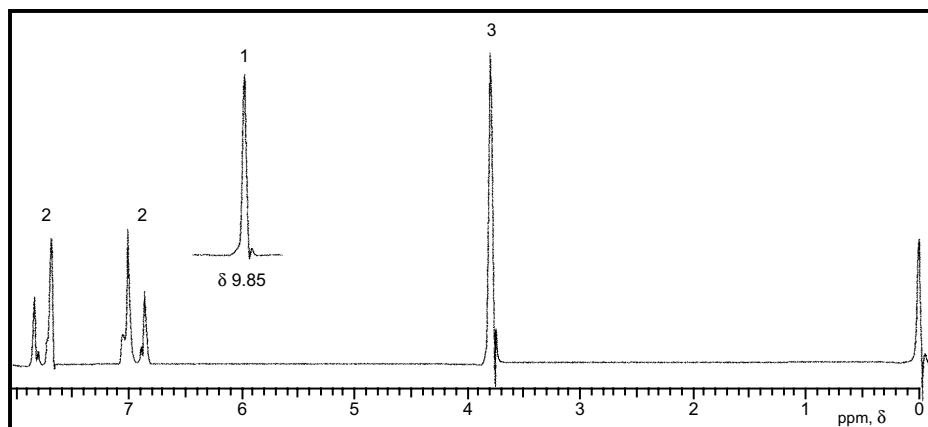


Compound 51 is a neutral, high-boiling liquid (boiling point 248 °C), that is easily oxidized to give a compound which is acidic. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 70.57; H, 5.92; O, 23.50.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

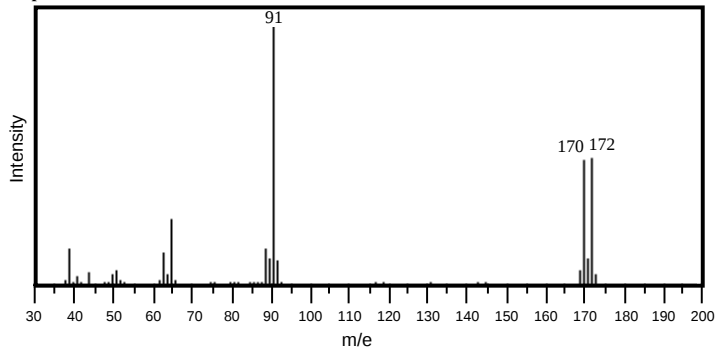
doublet, 190.0 ppm
singlet, 167.8 ppm
doublet, 130.7 ppm
singlet, 129.0 ppm
doublet, 114.6 ppm
quartet, 56.0 ppm

Structure:

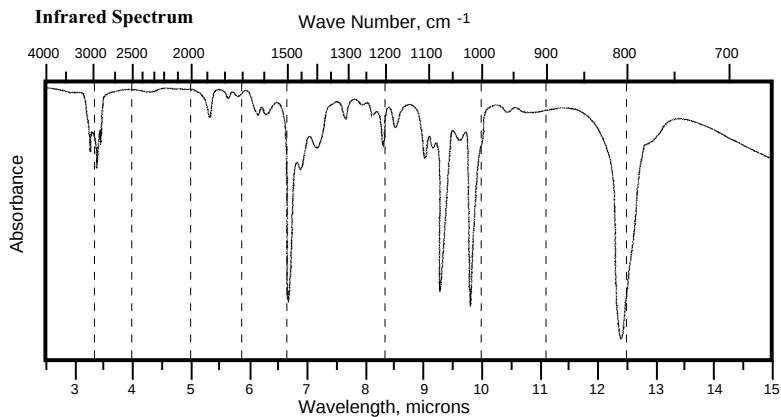
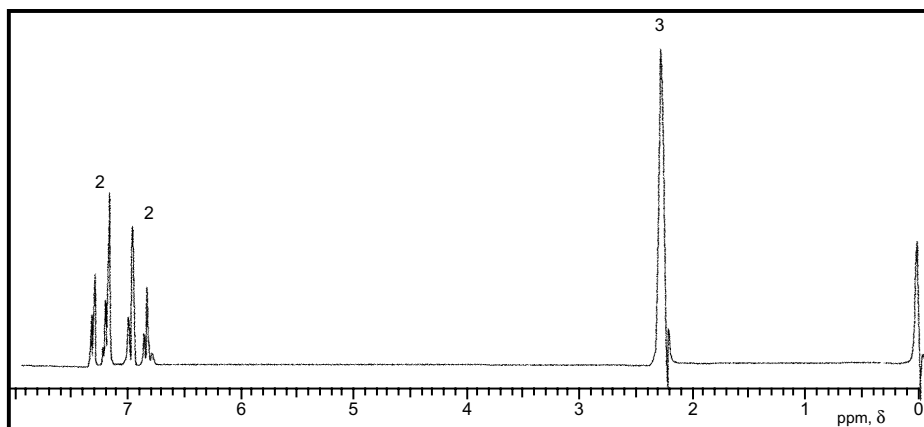


Compound 52 is a low-melting solid (melting point 26-29 °C), that can be prepared by the reaction of **Compound 13** with Br₂/FeBr₃. The Mass, IR, and ¹H NMR spectra, along with ¹³C NMR data, are given below. **Elemental Analysis:** C, 49.16; H, 4.13; contains halogen.

Mass Spectrum



Infrared Spectrum

¹H NMR¹³C Spectral Data:

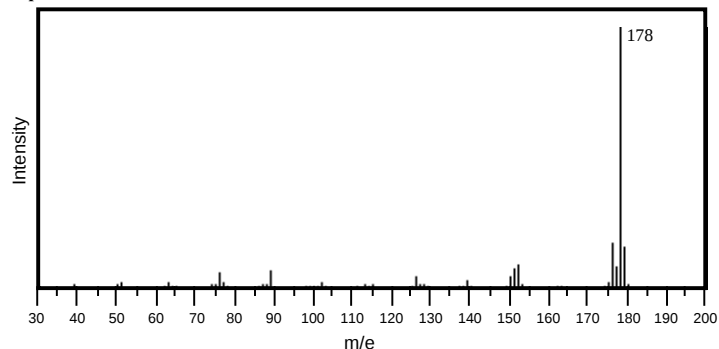
singlet, 136.7 ppm
 doublet, 131.7 ppm
 doublet, 131.4 ppm
 singlet, 120.1 ppm
 quartet, 20.9 ppm

Structure:

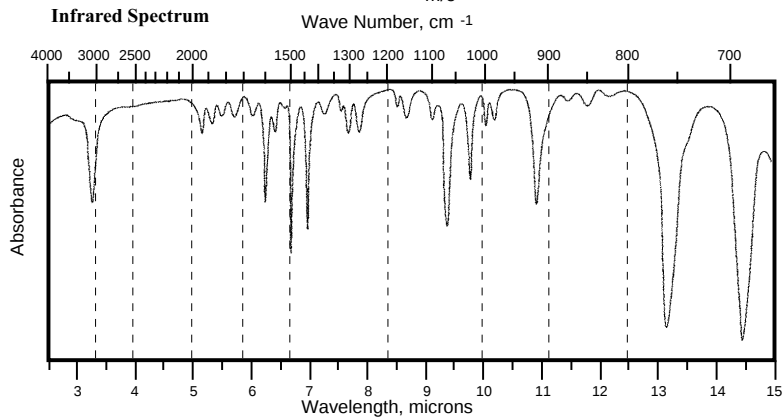
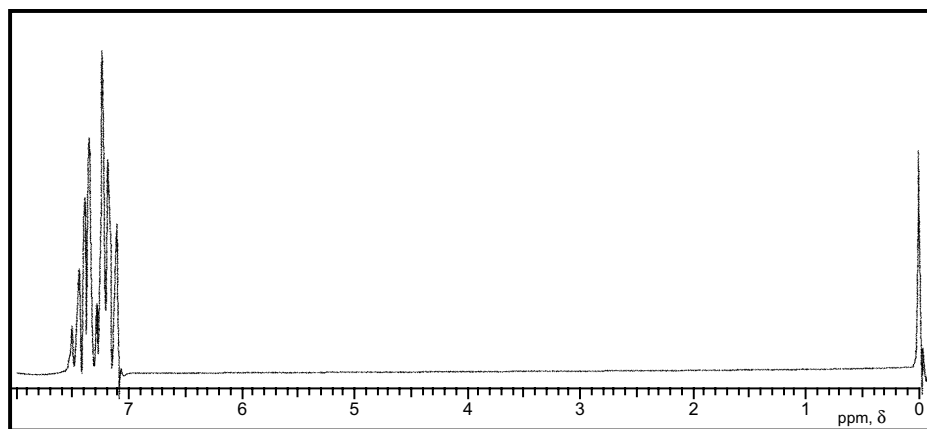


Compound 53 is a low-melting solid (melting point 64°C), which rapidly adds two moles of hydrogen gas in the presence of Pt/C. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. The stretching vibration for the functional group does not appear in the IR because of symmetry. **Elemental Analysis:** C, 94.34; H, 5.66.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

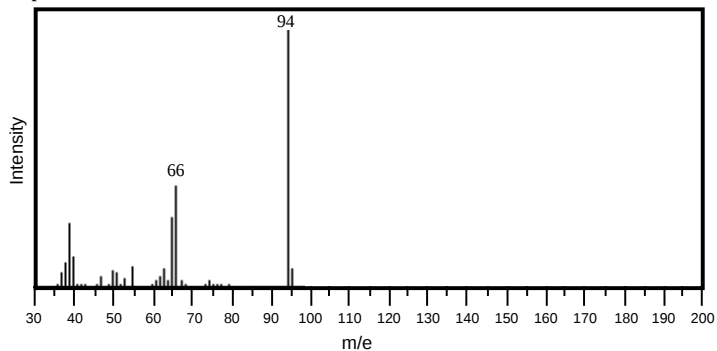
doublet, 132.1 ppm;
doublet, 128.2 ppm;
doublet, 128.1 ppm;
singlet, 122.3 ppm;
singlet, 91.9 ppm

Structure:

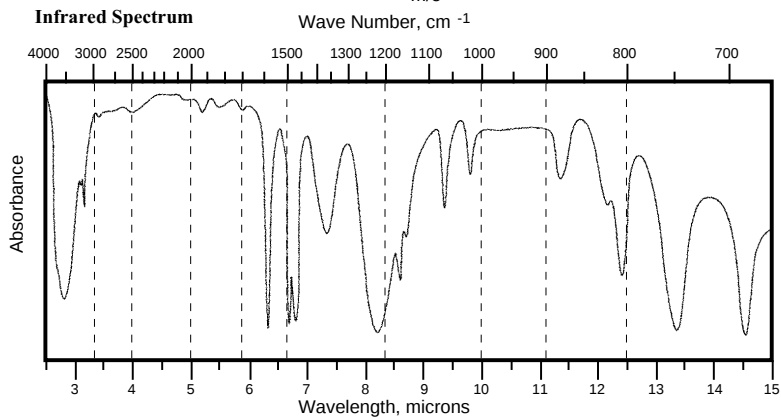
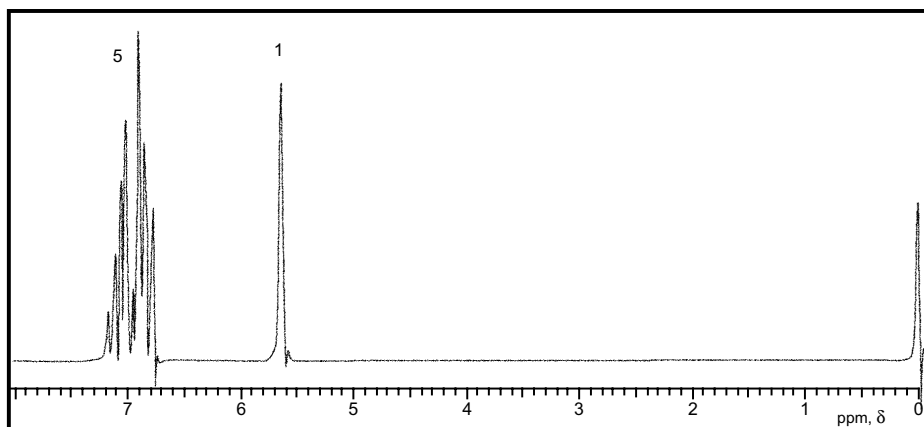


Compound 54 is a hygroscopic, low-melting solid (melting point 40 °C), that forms a corrosive, weakly acidic solution in water. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 76.57; H, 6.43; O, 17.00.

Mass Spectrum



Infrared Spectrum

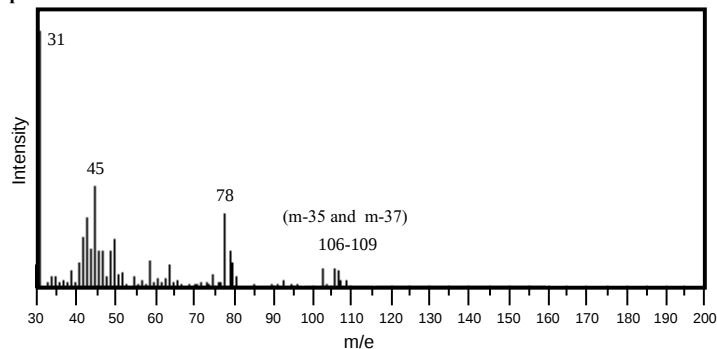
 ^1H NMR **^{13}C Spectral Data:**

singlet, 157.3 ppm
doublet, 129.9 ppm
doublet, 121.1 ppm
doublet, 115.7 ppm

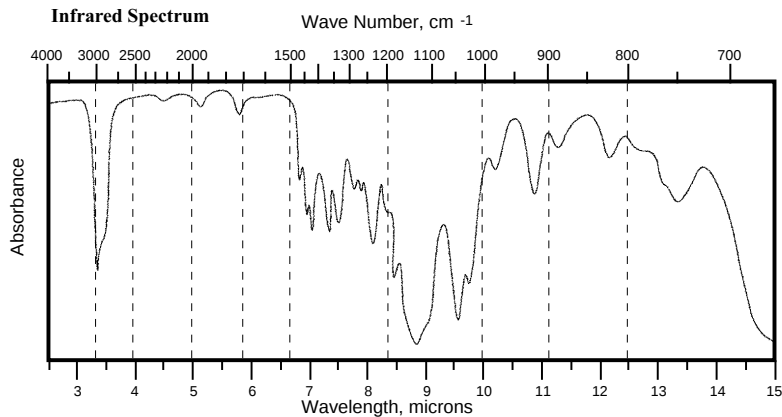
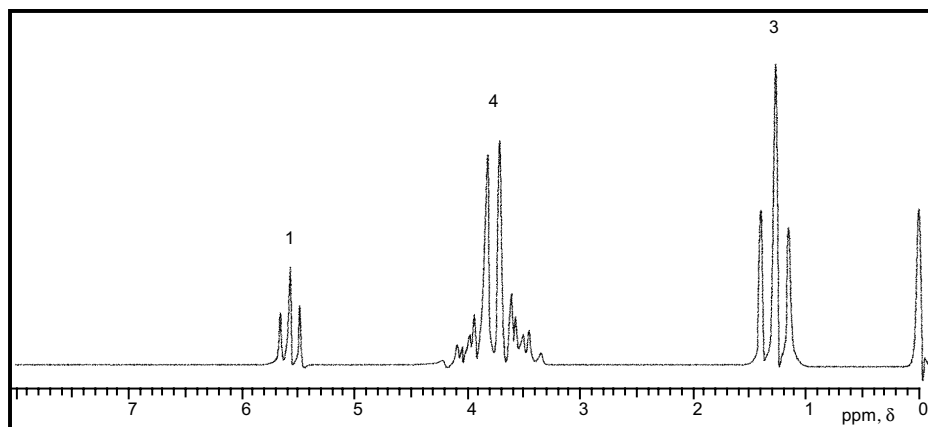
Structure:

Compound 55 is a liquid (boiling point 143° C) that can be prepared by the addition of halogen to an alkene. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. The molecular ion (an array of peaks at $m/e = 141$ -146) does not show in the Mass Spectrum. **Elemental Analysis:** C, 33.83; H, 4.97; O, 11.27; contains two moles of a halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

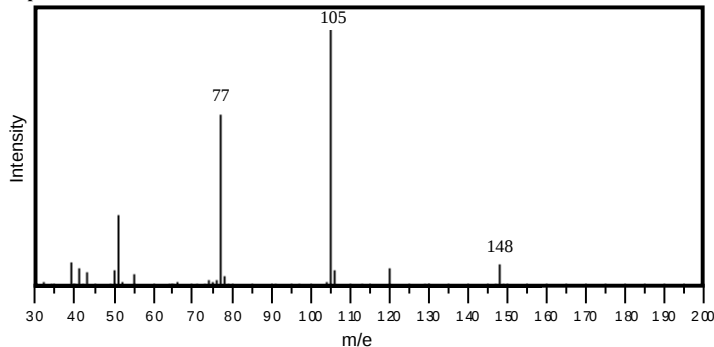
doublet, 97.3 ppm;
triplet, 61.0 ppm;
triplet, 54.3 ppm;
quartet, 14.7 ppm

Structure:

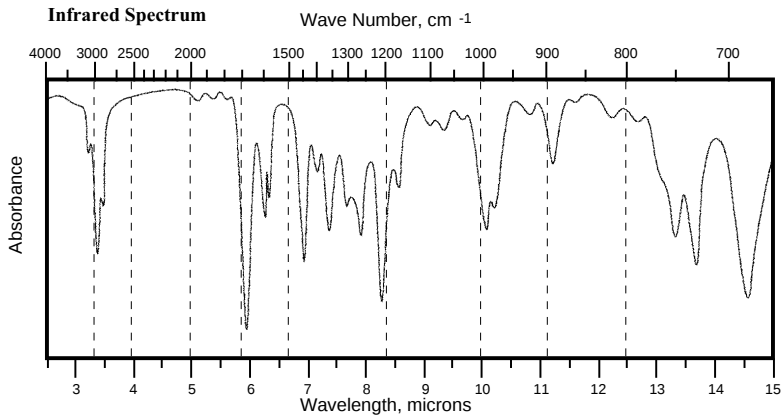
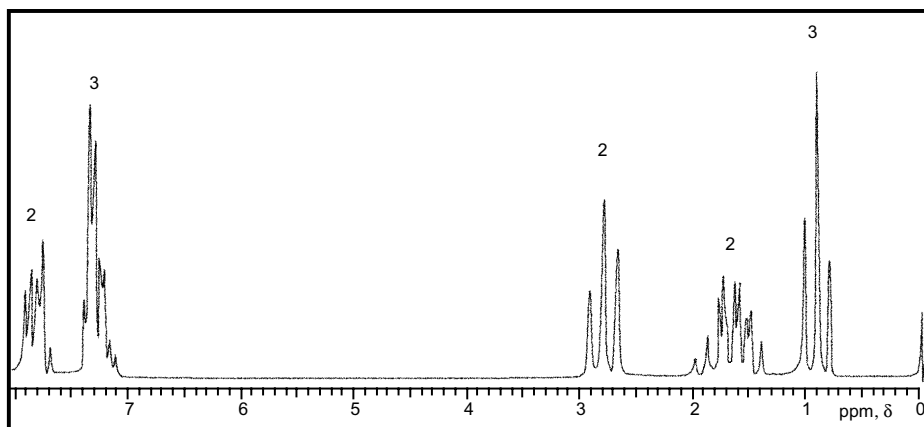


Compound 56 is a high-boiling liquid (boiling point 229° C) that does not react with I_2 in aqueous base to give a yellow precipitate of CHI_3 (a negative iodoform test). The Mass, IR, and 1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 81.04; H, 8.16; O, 10.80.

Mass Spectrum



Infrared Spectrum

 1H NMR ^{13}C Spectral Data:

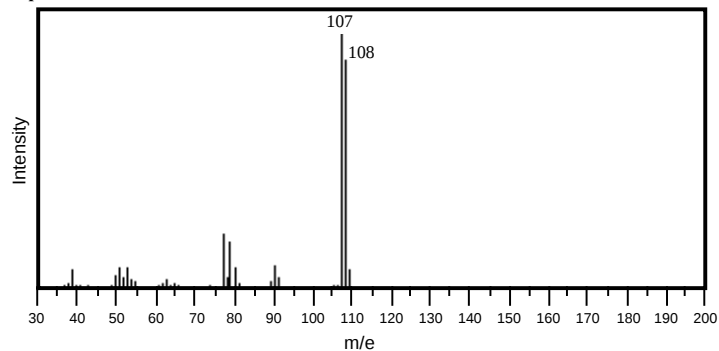
singlet, 197.6 ppm;
singlet, 137.4 ppm;
doublet, 132.9 ppm;
doublet, 128.6 ppm;
doublet, 128.4 ppm;
triplet, 48.9 ppm;
triplet, 19.8 ppm;
quartet, 13.5 ppm

Structure:

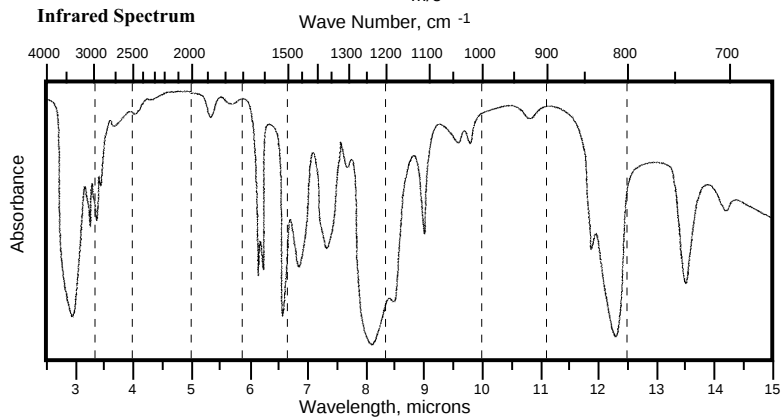
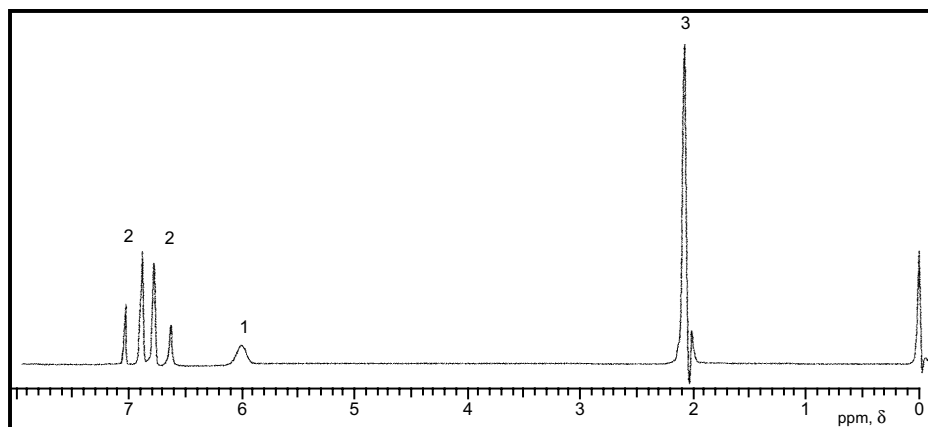


Compound 57 is a low-melting solid (melting point 32-34 °C), that is soluble in dilute aqueous base, but precipitates on acidification. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 77.75; H, 7.46; O, 14.80.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

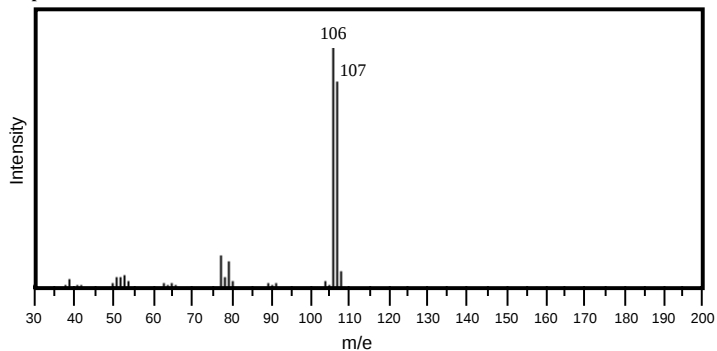
singlet, 154.3 ppm
 doublet, 130.6 ppm
 singlet, 130.3 ppm
 doublet, 115.6 ppm
 quartet, 22.0 ppm

Structure:

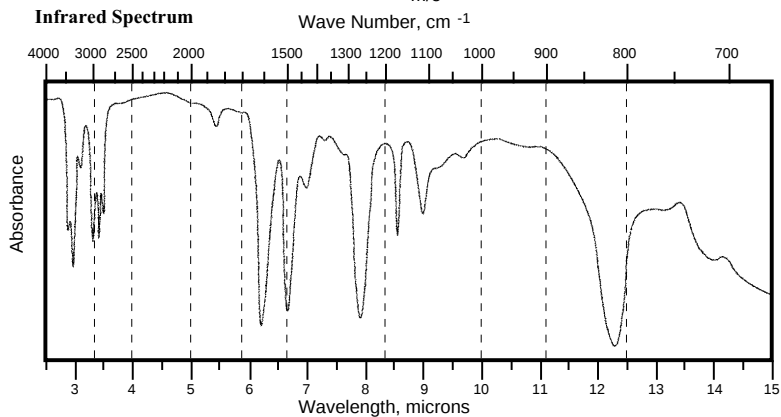
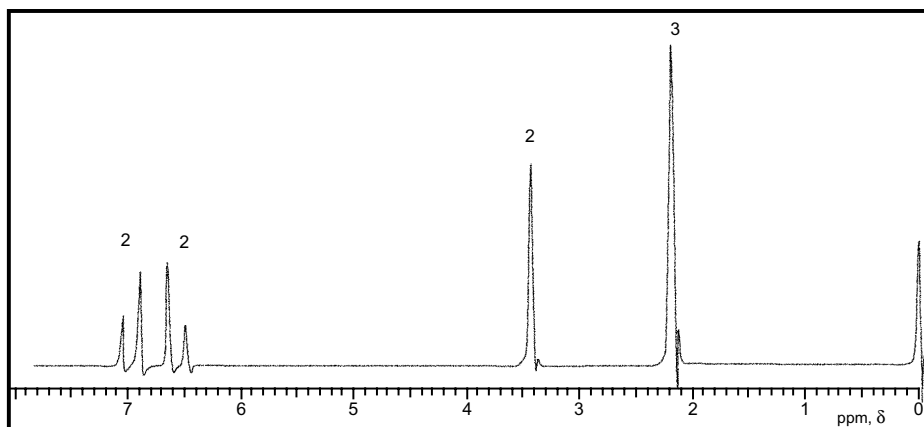


Compound 58 is a low melting solid (melting point 41–44 °C), that is soluble in dilute aqueous acid, but precipitates on neutralization. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below; the peak at 3.4 ppm in the ^1H NMR disappears if the compound is exposed to D_2O . **Elemental Analysis:** C, 78.46; H, 8.47; N, 13.07.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

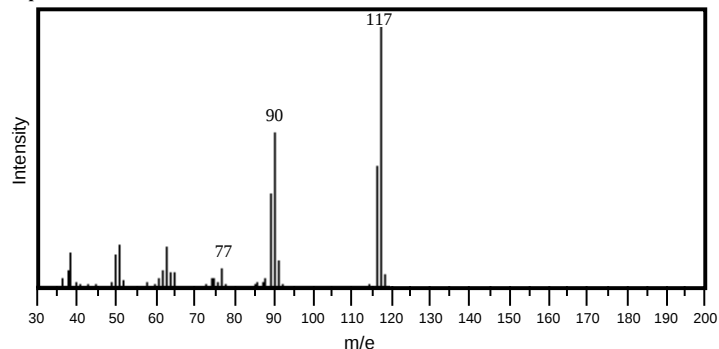
singlet, 143.7 ppm
 doublet, 130.0 ppm
 singlet, 127.7 ppm
 doublet, 115.0 ppm
 quartet, 22.0 ppm

Structure:

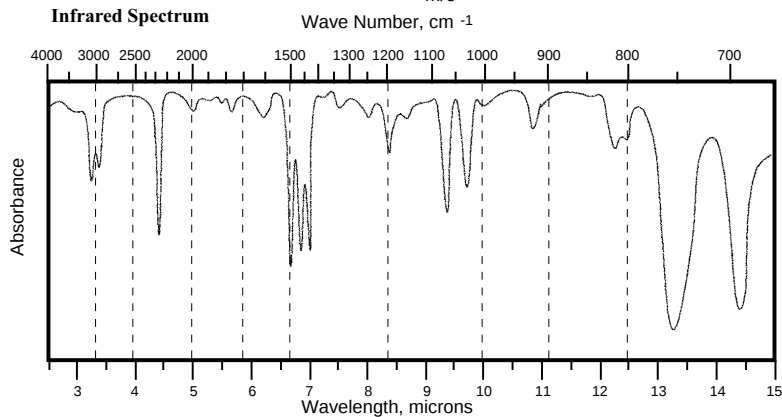
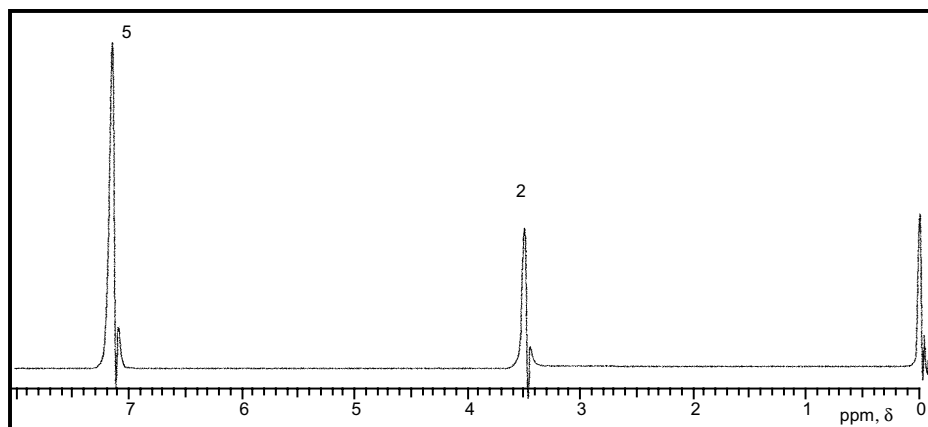


Compound 59 is a high-boiling neutral liquid (boiling point 234° C) that can be prepared by an S_N2 reaction between **Compound 9** and an inorganic anion. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 82.02; H, 6.02; N, 11.96.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

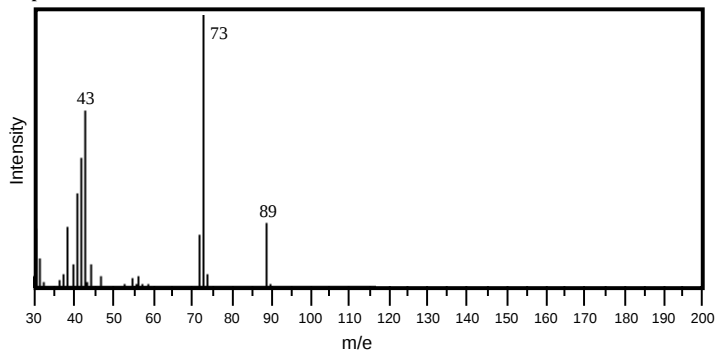
singlet, 130.1 ppm;
doublet, 129.0 ppm;
doublet, 127.8 ppm;
doublet, 127.7 ppm;
singlet, 117.7 ppm;
triplet, 26.3 ppm

Structure:

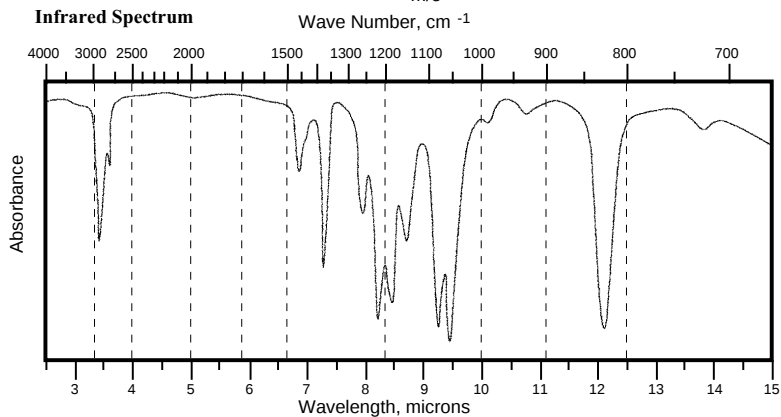
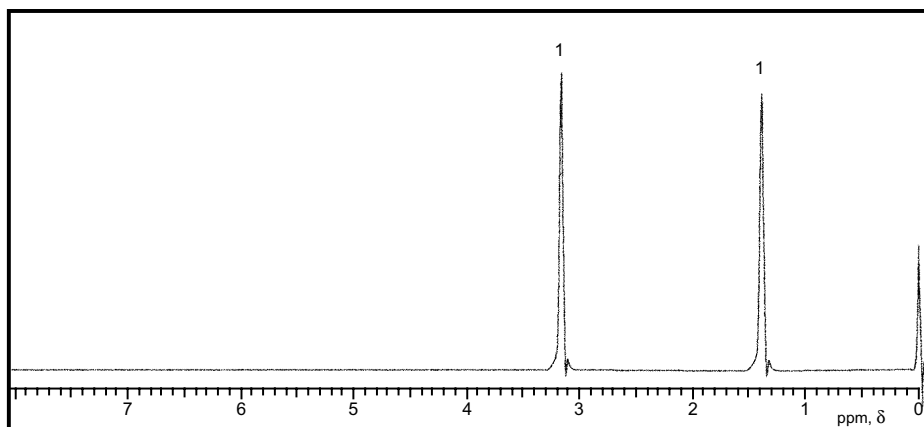


Compound 60 is a liquid (boiling point 83 °C), that can be prepared from **Compound 1** by reaction with acidic, anhydrous methanol. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 57.66; H, 11.61; O, 30.72.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

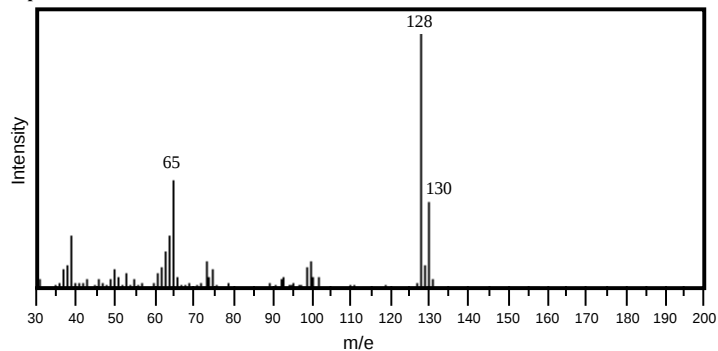
singlet, 119.0 ppm
quartet, 45.2 ppm
quartet, 32.5 ppm

Structure:

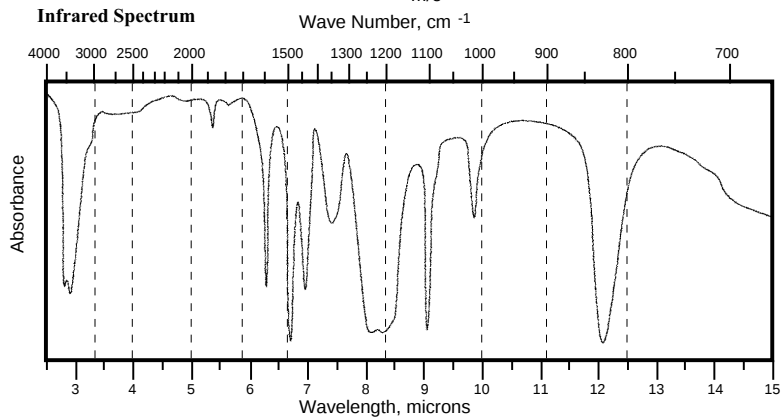
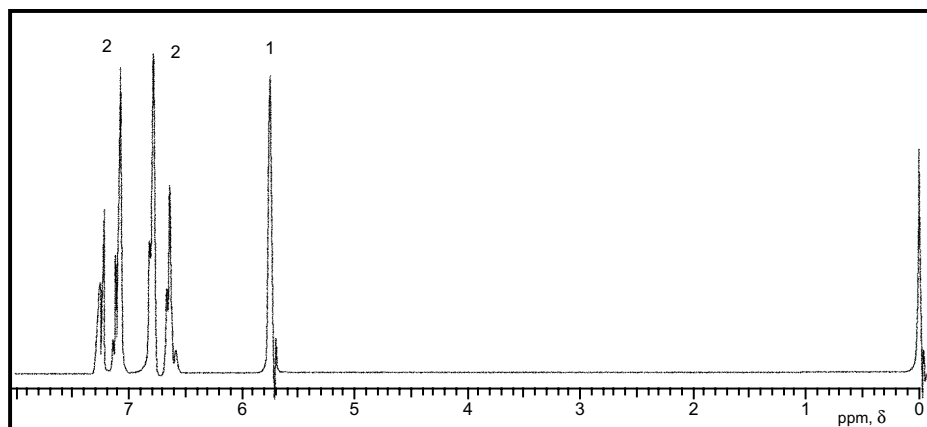


Compound 61 is a low-melting solid (melting point 40–42 °C), that will react with Br_2 in CCl_4 to give an addition compound and liberate two moles of HBr . The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 56.06; H, 3.92; O, 12.45; contains halogen.

Mass Spectrum



Infrared Spectrum

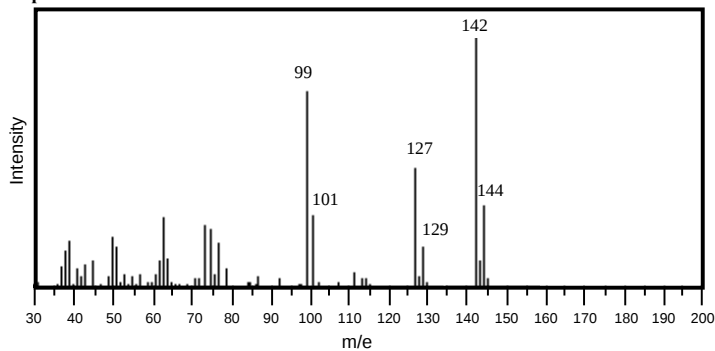
 ^1H NMR **^{13}C Spectral Data:**

singlet, 155.4 ppm
doublet, 130.3 ppm
singlet, 126.4 ppm
doublet, 117.1 ppm

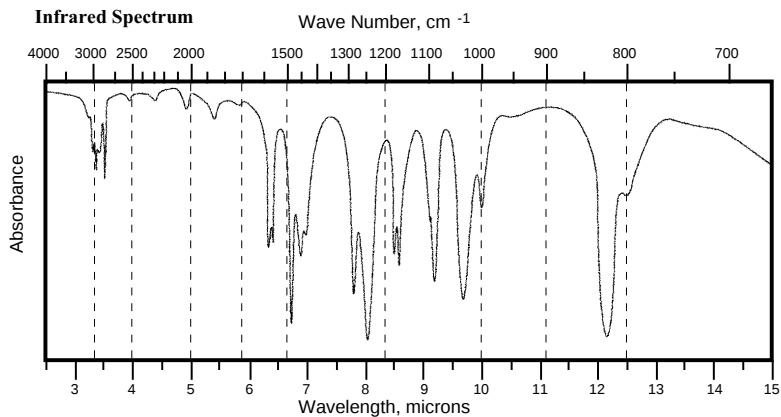
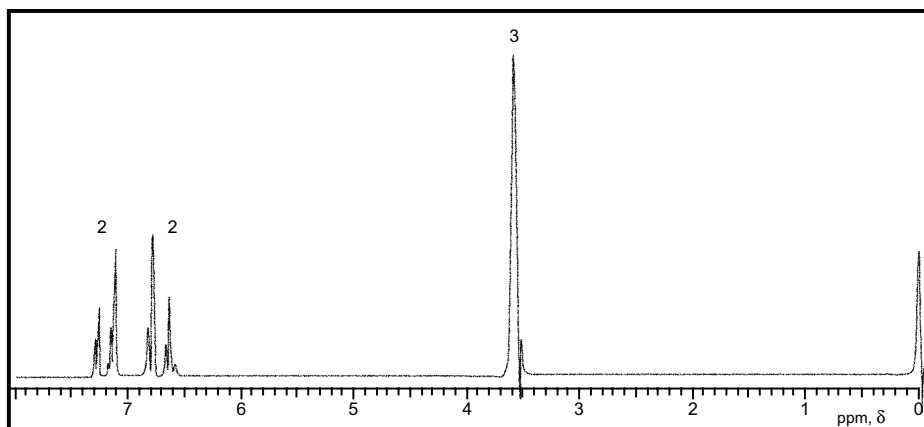
Structure:

Compound 62 is a high-boiling liquid (boiling point 202 °C), that can be prepared from the reaction between the anion of **Compound 61** and iodomethane. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 58.97; H, 4.95; O, 11.22 ; contains halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

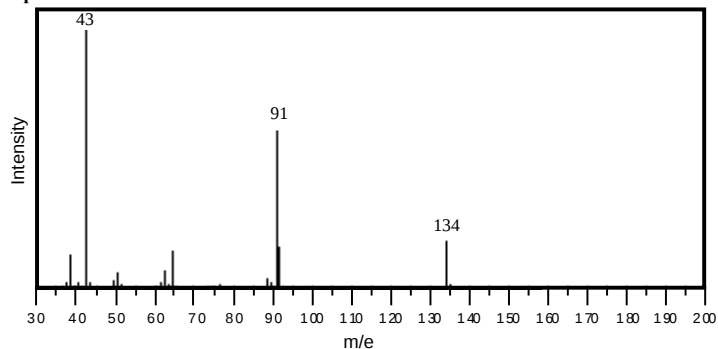
singlet, 160.1 ppm
 doublet, 129.9 ppm
 singlet, 126.1 ppm
 doublet, 115.5 ppm
 quartet, 56.0 ppm

Structure:

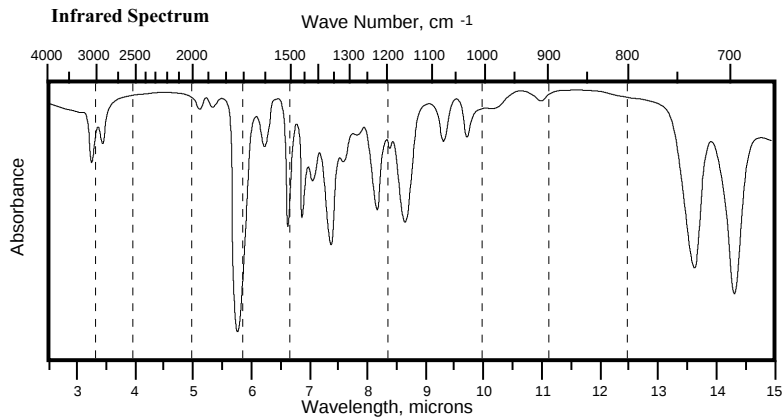
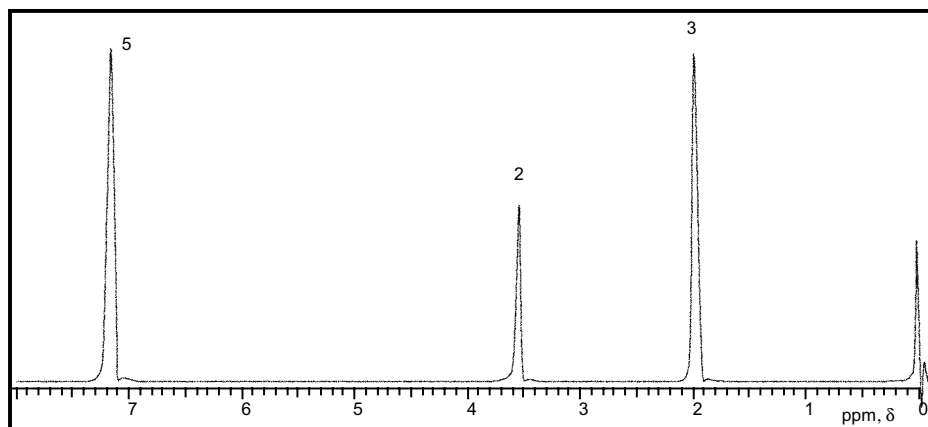


Compound 63 is a high-boiling liquid (boiling point 217° C) that reacts with I_2 in aqueous base to give a yellow precipitate of CHI_3 (the iodoform test). This compound can be prepared by the reaction between **Compound 59** and CH_3MgBr in ether solvent, followed by work-up in aqueous acid. The Mass, IR, and 1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 80.56; H, 7.51; O, 11.92.

Mass Spectrum



Infrared Spectrum

 1H NMR ^{13}C Spectral Data:

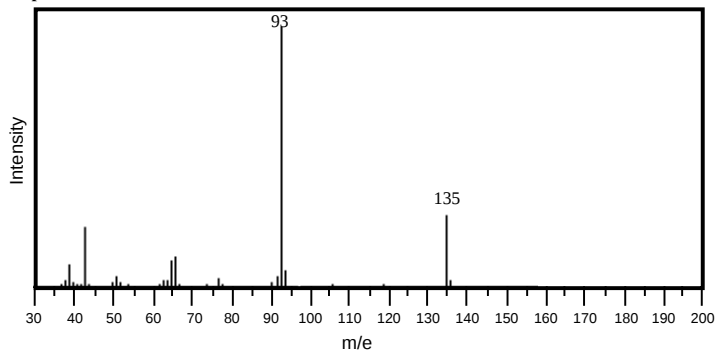
singlet, 207.1 ppm;
singlet, 138.8 ppm;
doublet, 128.6 ppm;
doublet, 128.3 ppm;
doublet, 125.8 ppm;
triplet, 51.3 ppm;
quartet, 24.4 ppm

Structure:

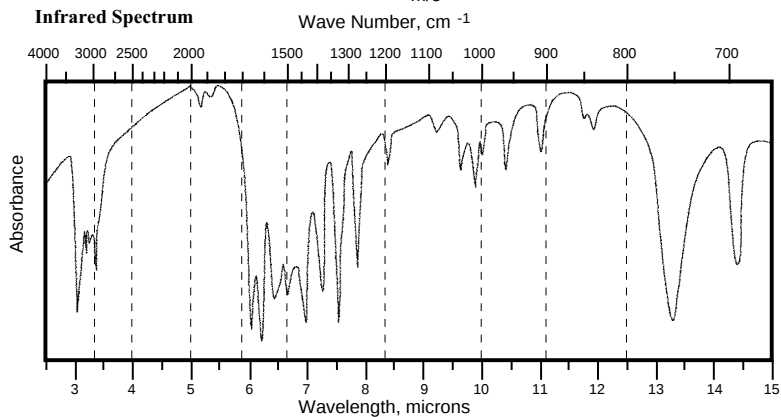
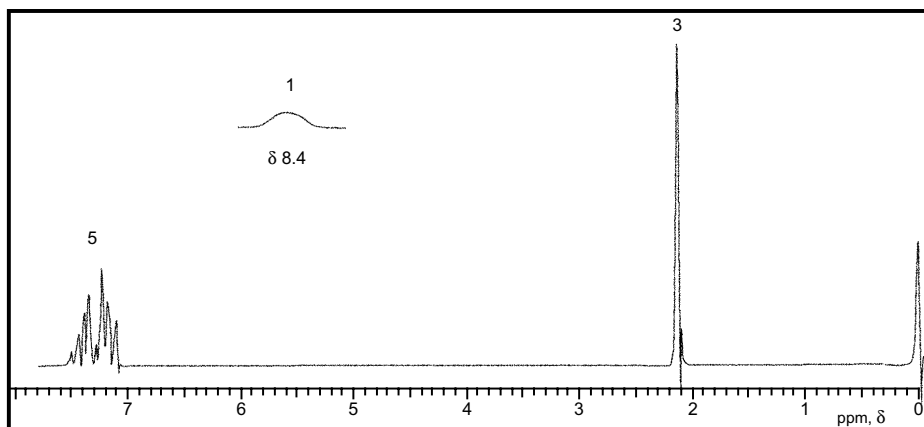


Compound 64 is a solid (melting point 114 °C), that can be prepared by the reaction between aniline and acetic anhydride. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 71.09; H, 6.71; N, 10.36; O, 11.84.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

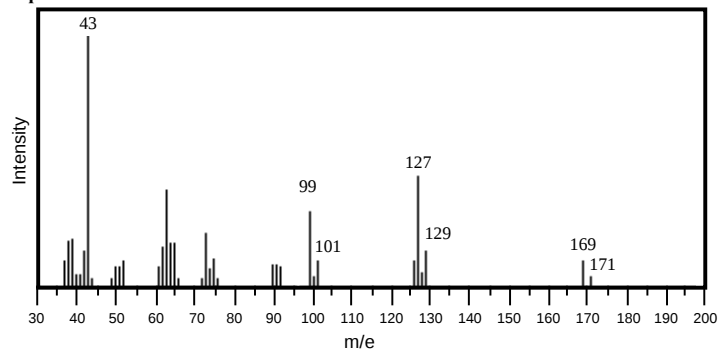
singlet, 168.2 ppm
singlet, 140.8 ppm
doublet, 128.7 ppm
doublet, 124.1 ppm
doublet, 120.4 ppm
quartet, 14.6 ppm

Structure:

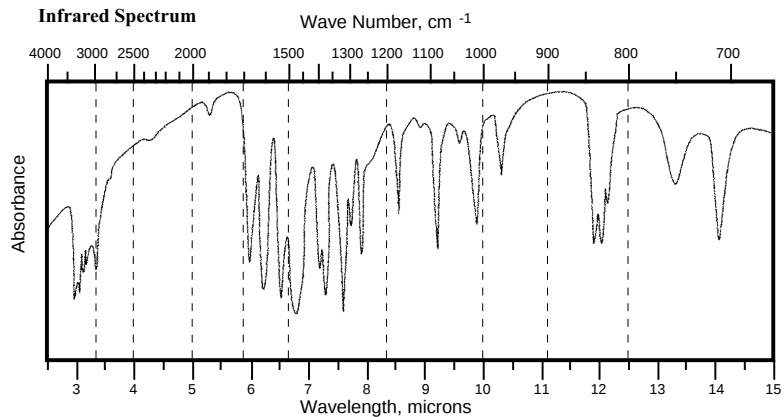
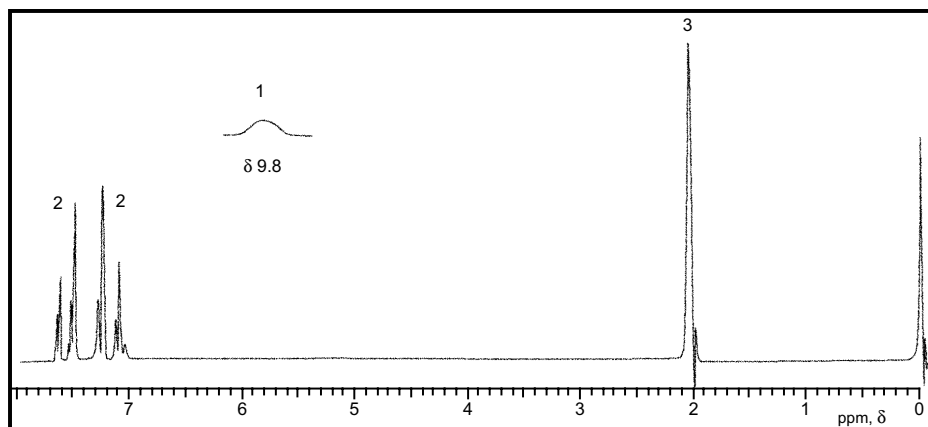


Compound 65 is a solid (melting point 177-179 °C), that can be prepared by the reaction of **Compound 64** with $\text{Cl}_2/\text{FeCl}_3$. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 56.65; H, 4.75; N, 8.26; O, 9.43; contains halogen.

Mass Spectrum



Infrared Spectrum

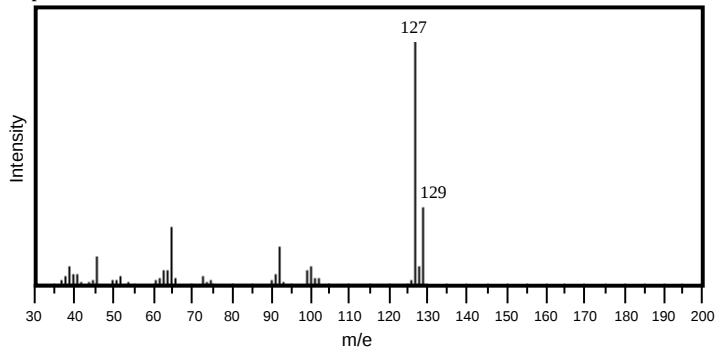
 ^1H NMR **^{13}C Spectral Data:**

singlet, 168.2 ppm
singlet, 138.9 ppm
singlet, 129.4 ppm
doublet, 129.1 ppm
doublet, 121.8 ppm
quartet, 17.6 ppm

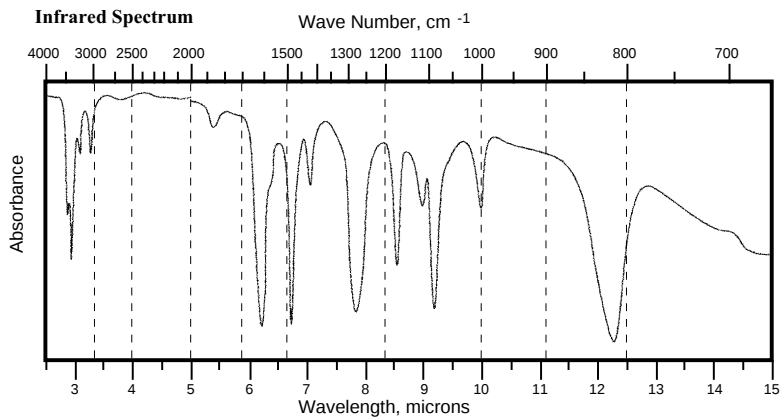
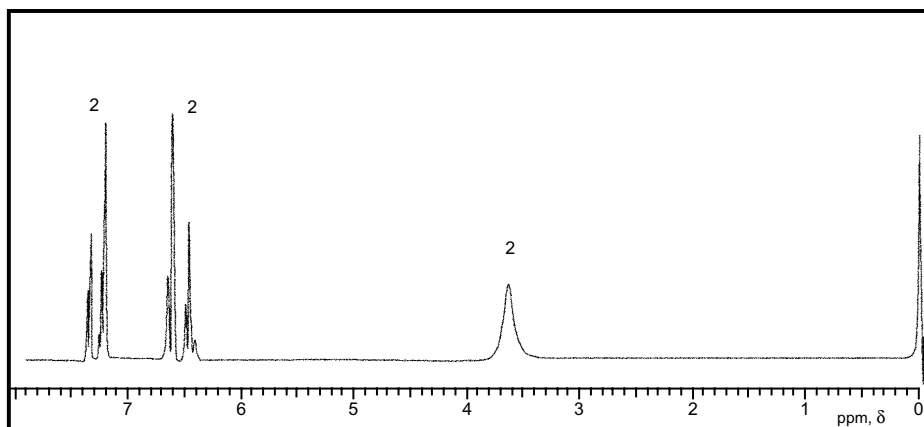
Structure:

Compound 66 is a solid (melting point 69-72 °C), that can be prepared by the alkaline hydrolysis of **Compound 65**; this compound, however, cannot be prepared by direct reaction between aniline and $\text{Cl}_2/\text{FeCl}_3$. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 56.49; H, 4.74; N, 10.98; contains halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

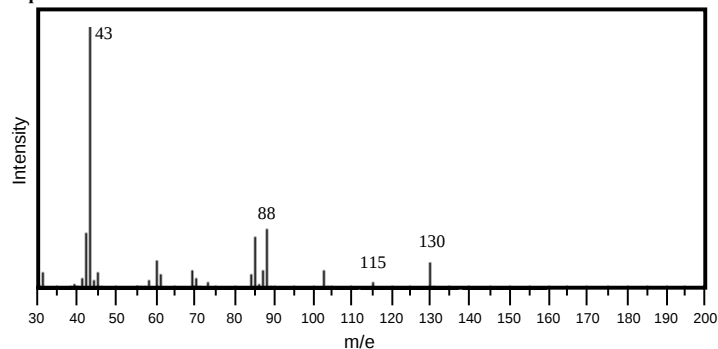
singlet, 144.8 ppm
doublet, 129.7 ppm
singlet, 123.8 ppm
doublet, 116.5 ppm

Structure:

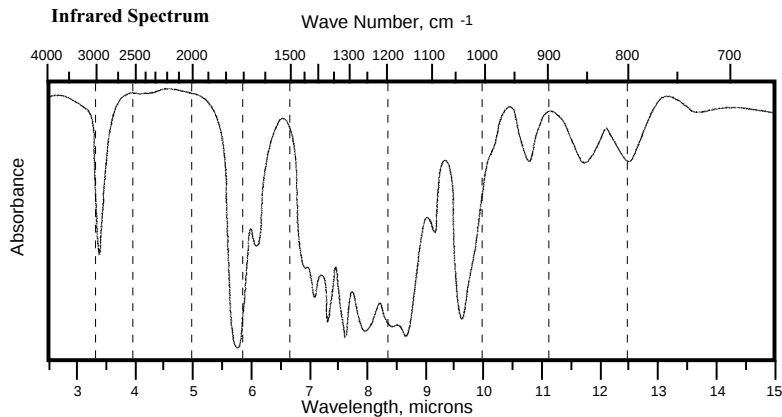
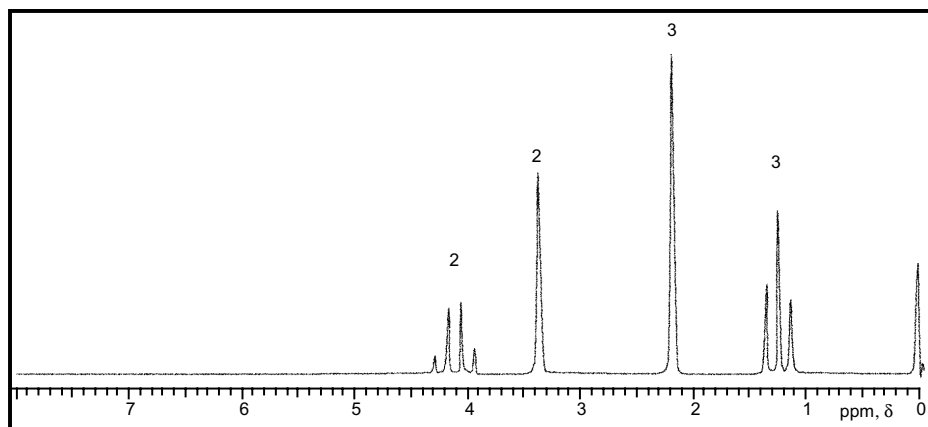


Compound 67 is a high-boiling liquid (boiling point 180° C) that reacts with I_2 in aqueous base to give a yellow precipitate of CHI_3 (the iodoform test). The compound is readily prepared by the condensation of two moles of ethyl acetate in the presence of ethanol/ethoxide anion. The Mass, IR, and 1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 55.37; H, 7.74; O, 36.88.

Mass Spectrum



Infrared Spectrum

 1H NMR ^{13}C Spectral Data:

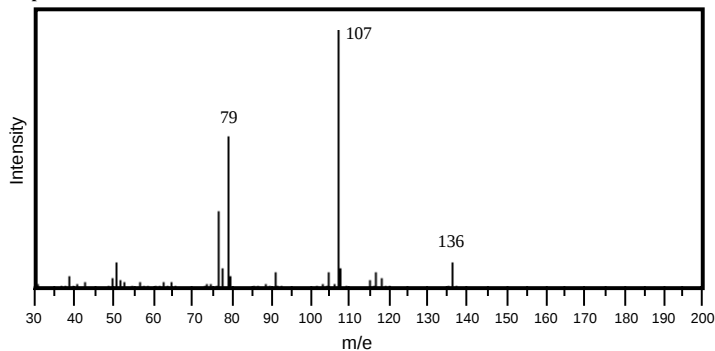
singlet, 207.1 ppm;
singlet, 172.0 ppm;
triplet, 59.2 ppm;
triplet, 46.6 ppm;
quartet, 24.2 ppm;
quartet, 13.6 ppm

Structure:

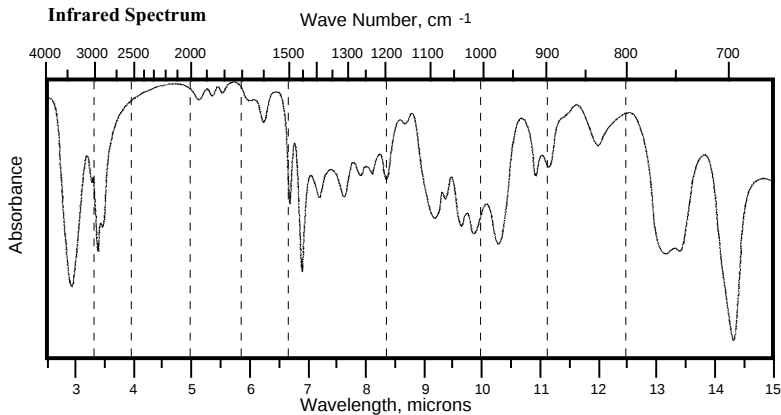
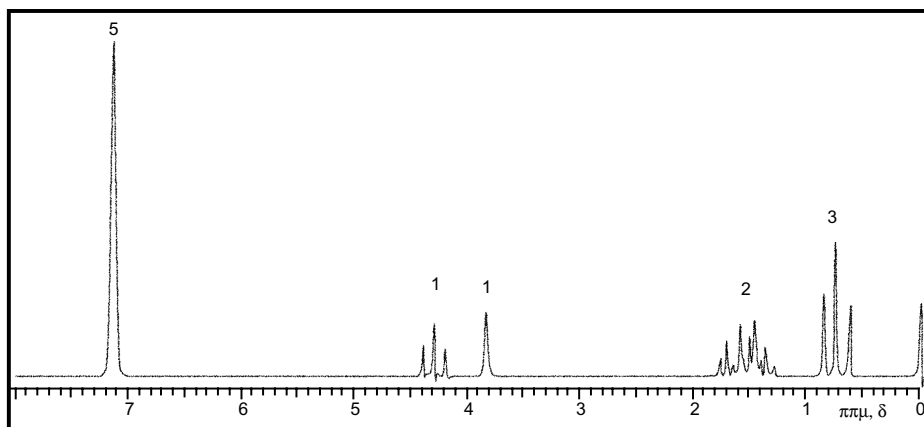


Compound 68 is a high-boiling, neutral liquid (boiling point 219° C). The peak at 4.3 ppm in the ^1H NMR disappears if the compound is exposed to D_2O . The compound can be readily prepared by the reaction of an aldehyde with phenylmagnesium bromide in ether. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 79.37; H, 8.88; O, 11.75.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

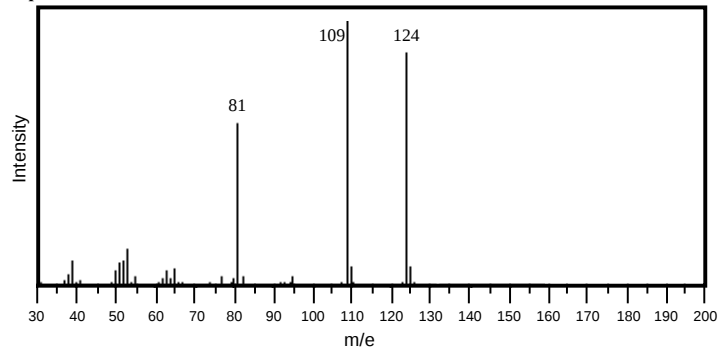
singlet, 138.8 ppm;
doublet, 128.6 ppm;
doublet, 128.3 ppm;
doublet, 125.8 ppm;
doublet, 92.0 ppm;
triplet, 35.3 ppm;
quartet, 7.4 ppm

Structure:

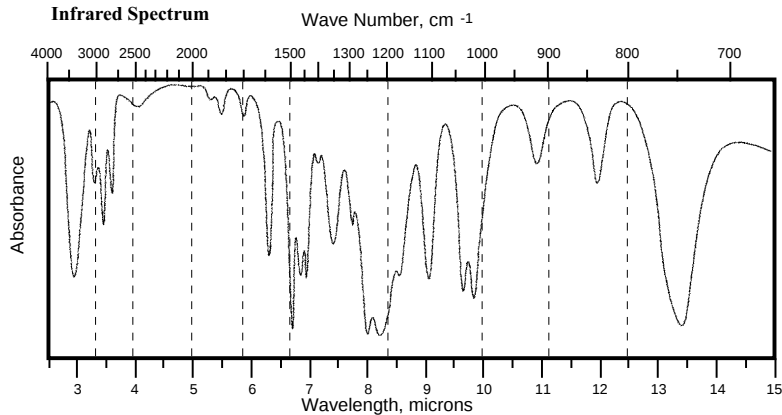
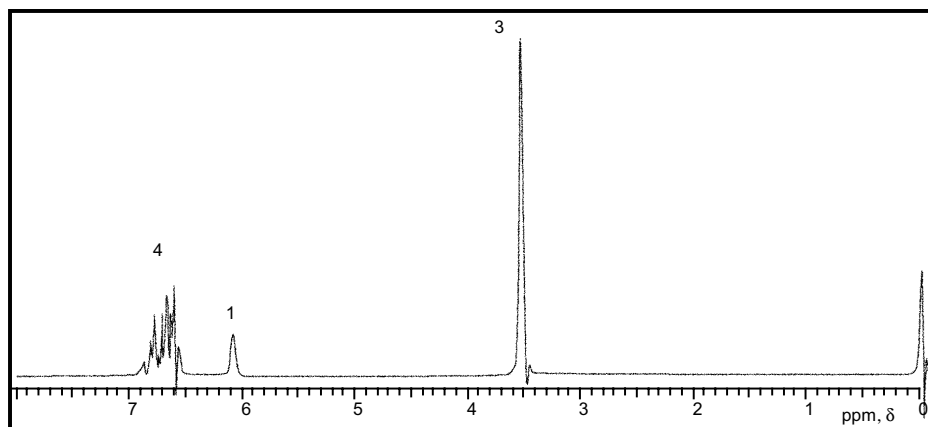


Compound 69 is a low-melting solid (melting point 28° C), that is a weak acid and rapidly adds bromine with the formation of HBr. Reaction of the anion of this compound with iodomethane gives a compound which has **one singlet** and **two doublets** in the arene region of the ^{13}C NMR, elucidating the substitution pattern of the parent compound. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 67.73; H, 6.50; O, 25.78.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

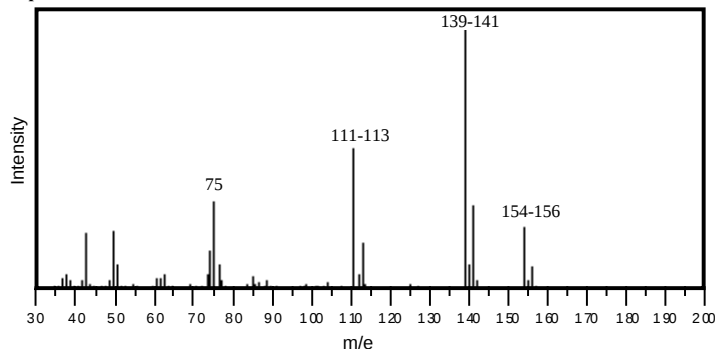
singlet, 149.2 ppm;
singlet, 142.9 ppm;
doublet, 122.2 ppm;
doublet, 122.1 ppm;
doublet, 116.7 ppm;
doublet, 115.5 ppm;
quartet, 56.3 ppm

Structure:

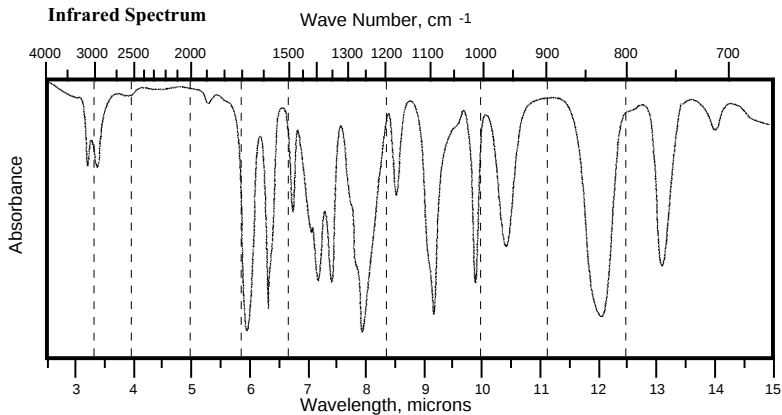
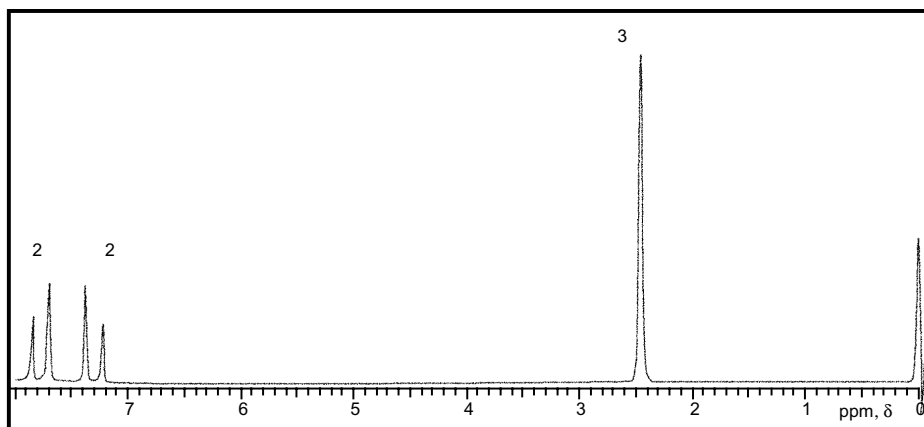


Compound 70 is a high-boiling liquid (boiling point 273° C) which reacts with I_2 in aqueous base to give a yellow precipitate of CHI_3 (the iodoform test). This compound can be readily prepared by the reaction of **Compound 6** with acetic anhydride in the presence of $AlCl_3$. The Mass, IR, and 1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 62.15; H, 4.56; O, 10.35; contains halogen.

Mass Spectrum



Infrared Spectrum

 1H NMR ^{13}C Spectral Data:

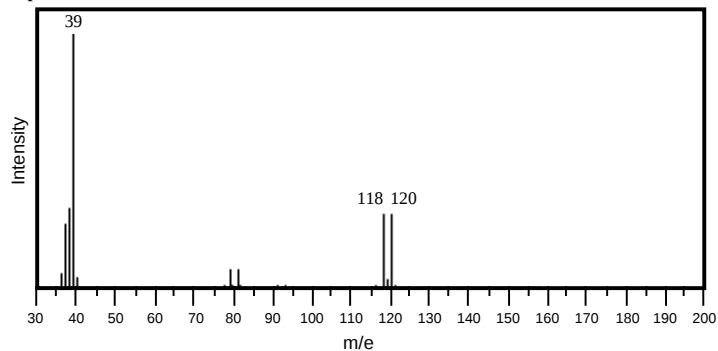
singlet, 196.5 ppm;
singlet, 151.1 ppm;
doublet, 129.4 ppm;
singlet, 127.4 ppm;
doublet, 115.0 ppm;
quartet, 27.0 ppm

Structure:

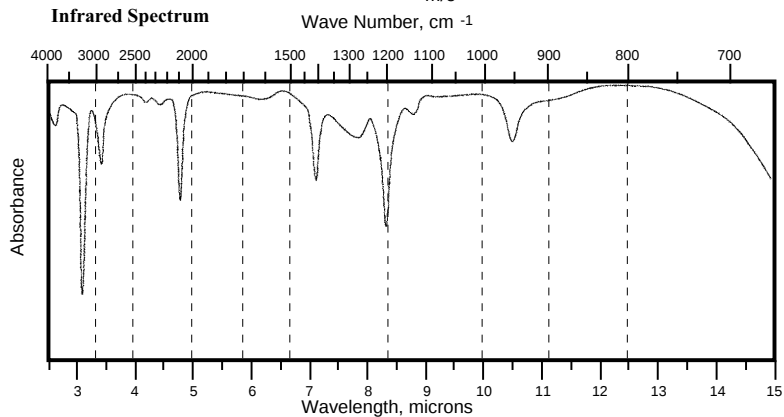
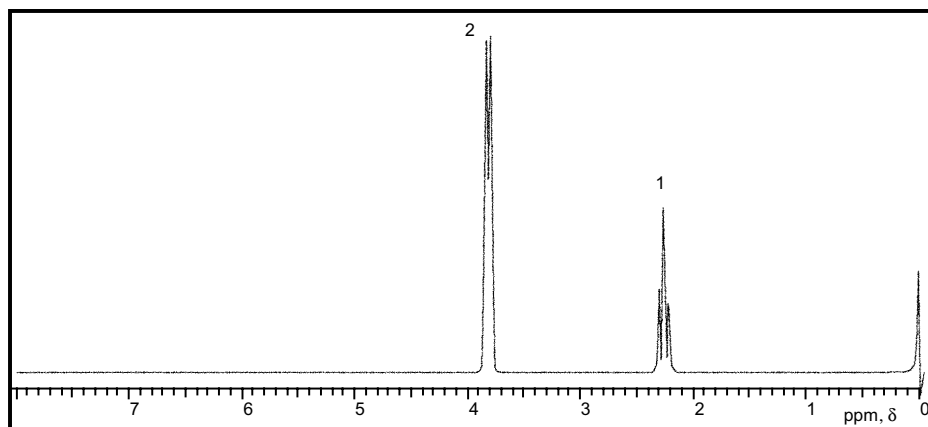


Compound 71 is a liquid (boiling point 89° C) which adds two moles of hydrogen gas in the presence of Pt/C. The compound is readily prepared by the free radical halogenation of propyne. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. Long-range coupling with $J \approx 2$ Hz is visible in the ^1H NMR. **Elemental Analysis:** C, 30.29; H, 2.54; contains halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

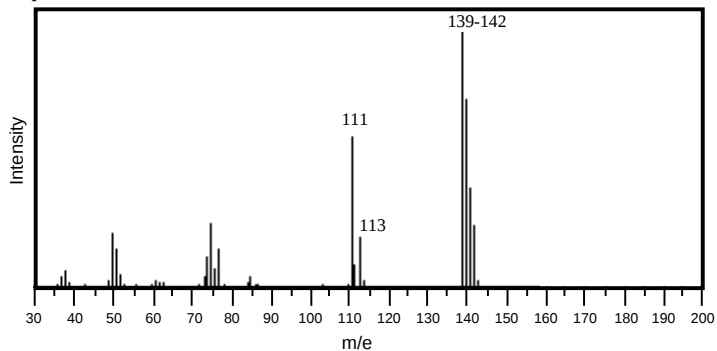
doublet, 68.1 ppm;
singlet, 80.3 ppm;
triplet, 22.6 ppm

Structure:

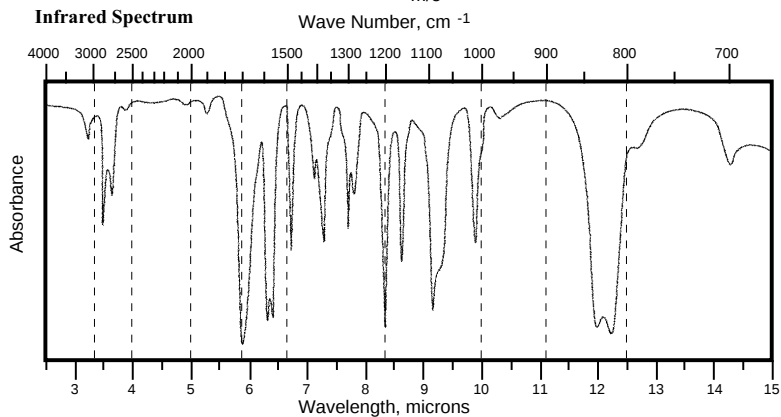
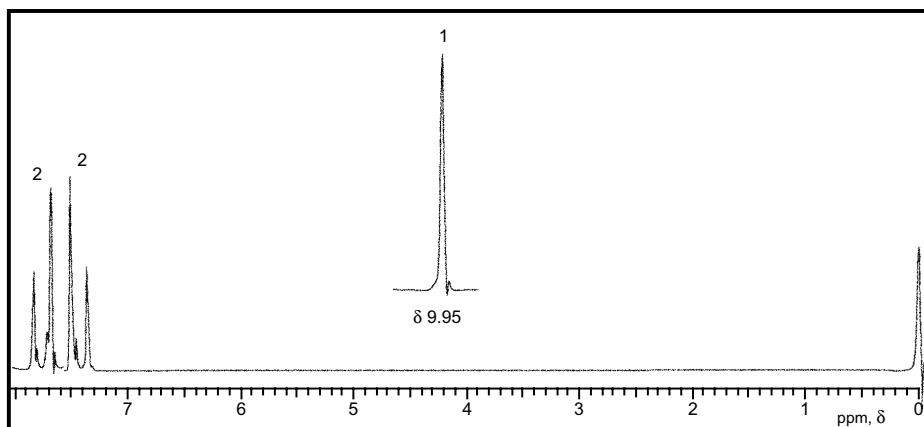


Compound 72 is a low-melting solid (melting point 46–48 °C), that reacts with aqueous hydroxylamine to form a crystalline oxime (melting point 110 °C). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 59.81; H, 3.59; O, 11.38; contains halogen.

Mass Spectrum



Infrared Spectrum

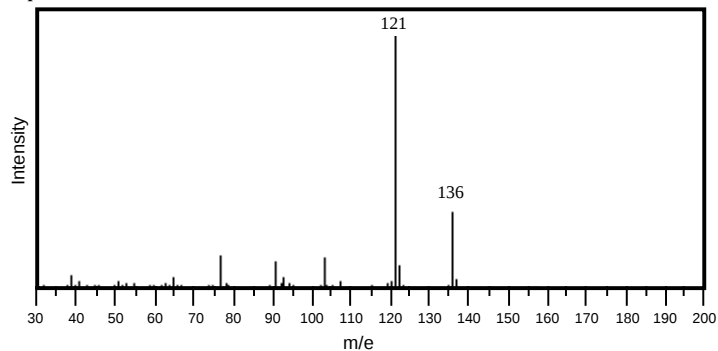
 ^1H NMR **^{13}C Spectral Data:**

doublet, 190.0 ppm
singlet, 139.6 ppm
singlet, 134.8 ppm
doublet, 131.1 ppm
doublet, 129.4 ppm

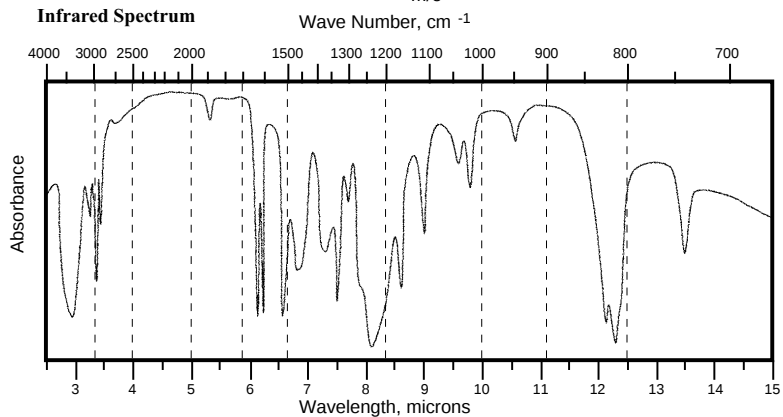
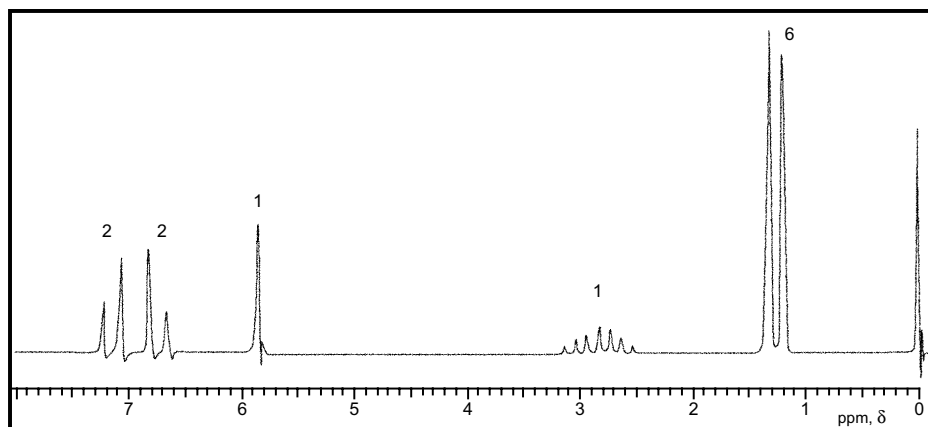
Structure:

Compound 73 is a solid (melting point 59-61 °C), that is soluble in dilute base, but precipitates on acidification. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 79.37; H, 8.88; O, 11.75.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

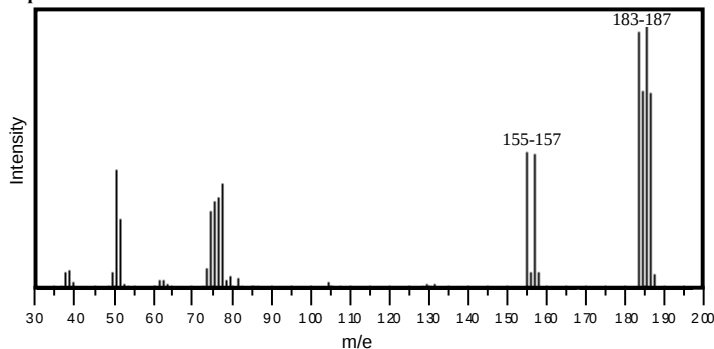
singlet, 154.5 ppm
singlet, 141.3 ppm
doublet, 127.7 ppm
doublet, 115.4 ppm
triplet, 40.2 ppm
quartet, 25.5 ppm

Structure:

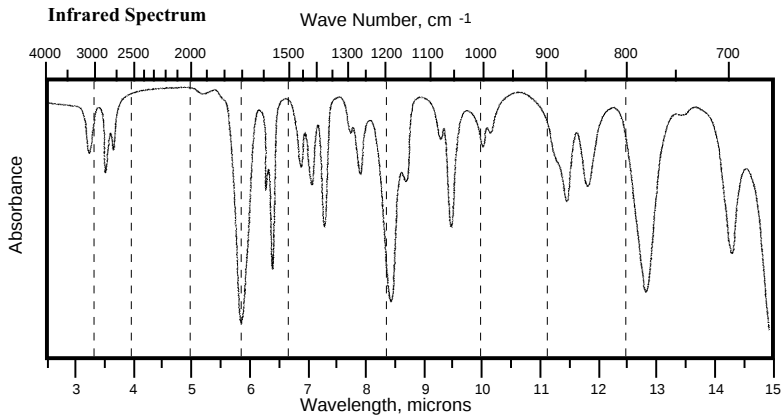
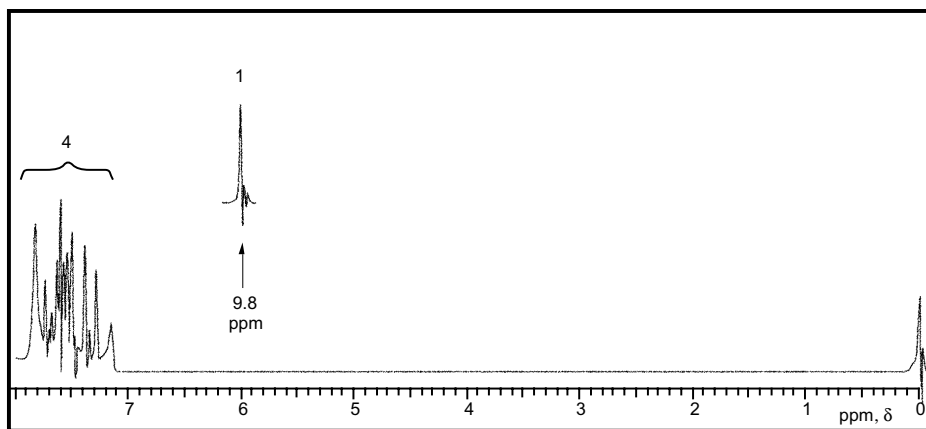


Compound 74 is a high-boiling liquid (boiling point 230° C) that reacts with Ag^+ ion in aqueous ammonia to form a “silver mirror” (the Tollens test). The compound can be prepared by a Friedel-Crafts bromination reaction; this functional group commonly shows an (m-1) peak in the Mass Spectrum. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 45.44; H, 2.72; O, 8.65; contains halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

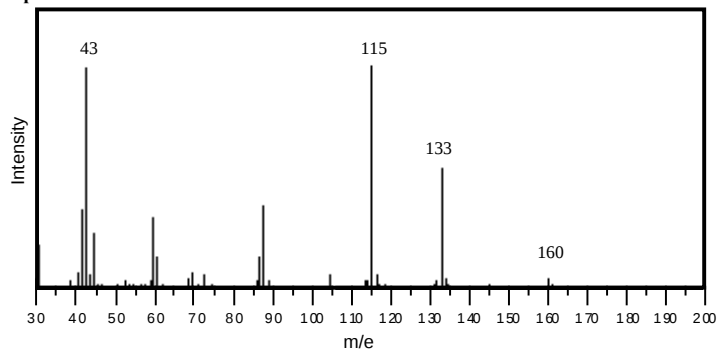
singlet, 190.0 ppm;
 doublet, 137.8 ppm;
 singlet, 137.4 ppm;
 doublet, 134.0 ppm;
 doublet, 133.2 ppm;
 doublet, 129.7 ppm;
 singlet, 116.0 ppm

Structure:

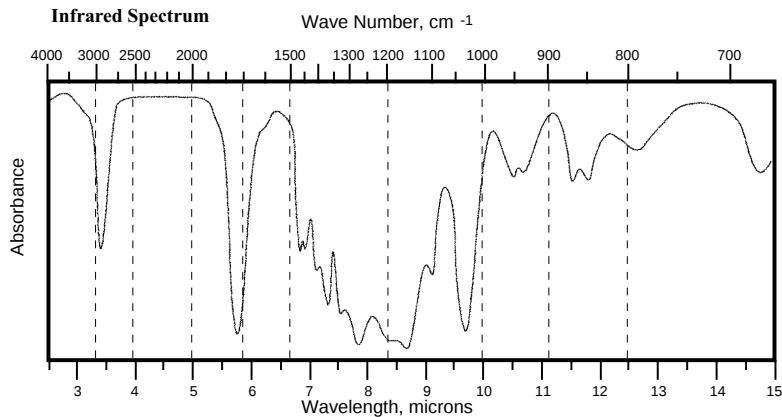
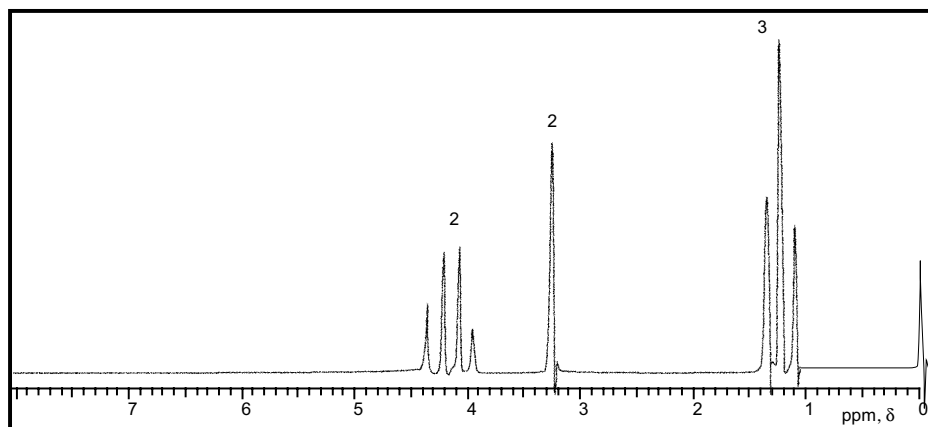


Compound 75 is a high-boiling liquid (boiling point 199° C), that reacts with alkyl halides in the presence of alkoxide to yield α -substitution products. Hydrolysis of this compound in dilute aqueous acid results in the loss of CO_2 and the formation of a simple organic acid. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 52.49; H, 7.55; O, 39.96

Mass Spectrum



Infrared Spectrum

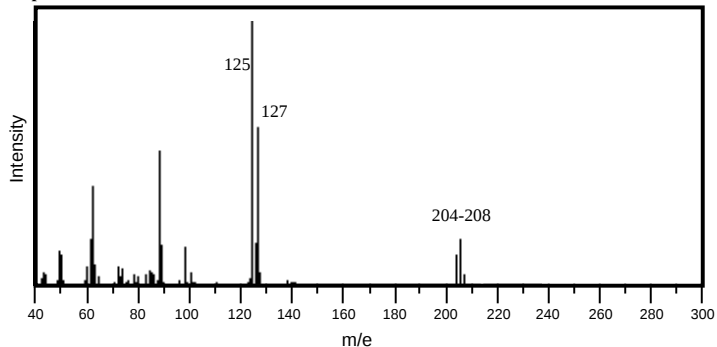
 ^1H NMR **^{13}C Spectral Data:**

singlet, 172.0 ppm;
triplet, 59.2 ppm;
triplet, 36.9 ppm;
quartet, 13.6 ppm

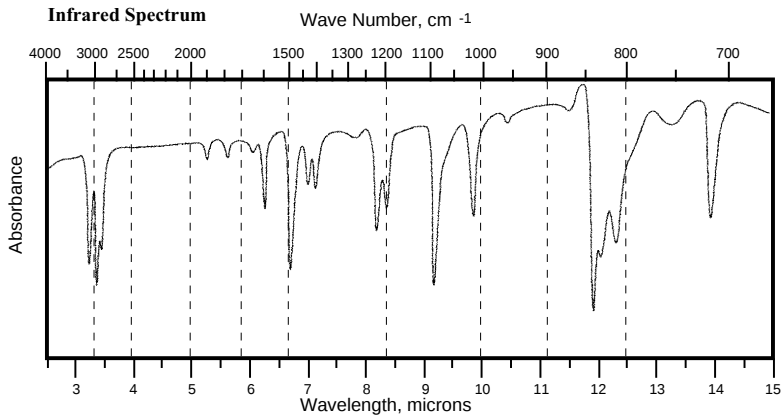
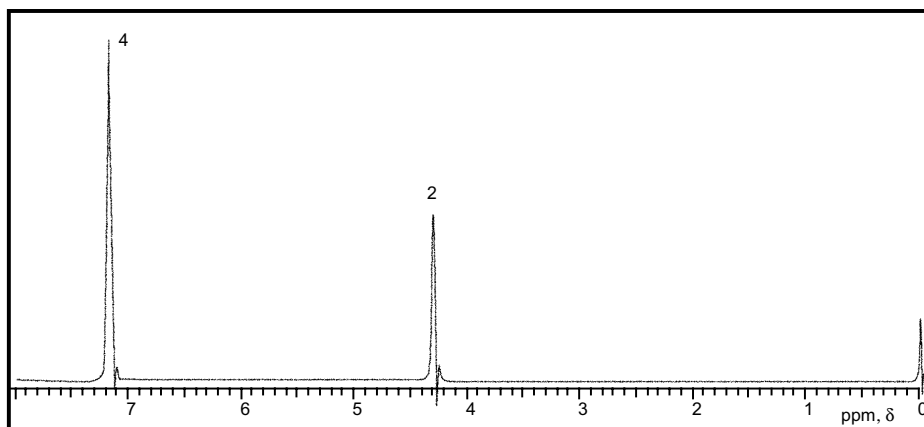
Structure:

Compound 76 is a low-melting solid (melting point 50° C), which contains two different halogens; alkoxide can displace only **one** of these, yielding an ether. In the 300 MHz ^1H NMR, the apparent singlet at 7.15 ppm is resolved into two, closely spaced, doublets. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 40.92; H, 2.94; contains two different halogens.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

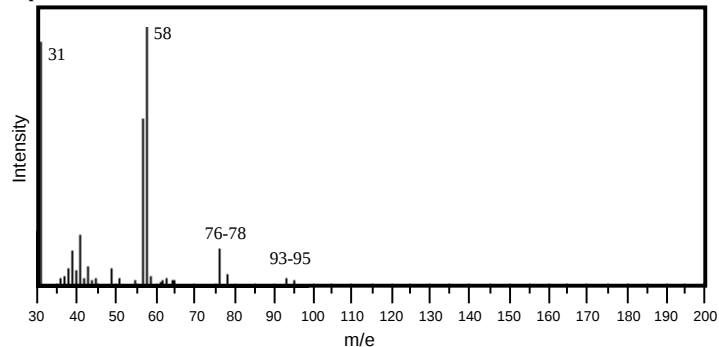
singlet, 146.0 ppm;
doublet, 129.8 ppm;
singlet, 120.1 ppm;
doublet, 114.3 ppm;
triplet, 29.3 ppm

Structure:

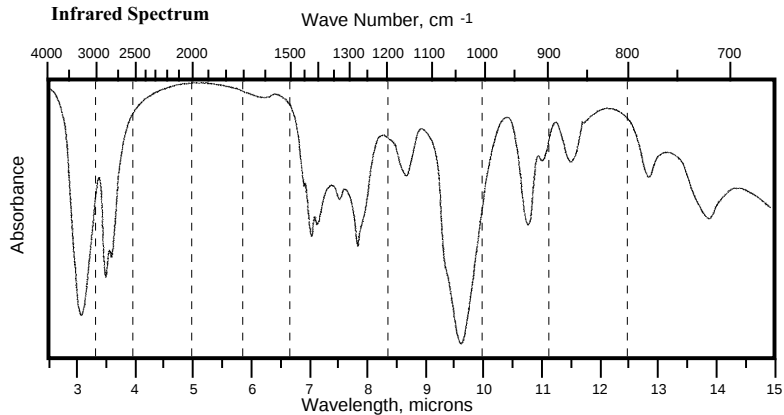
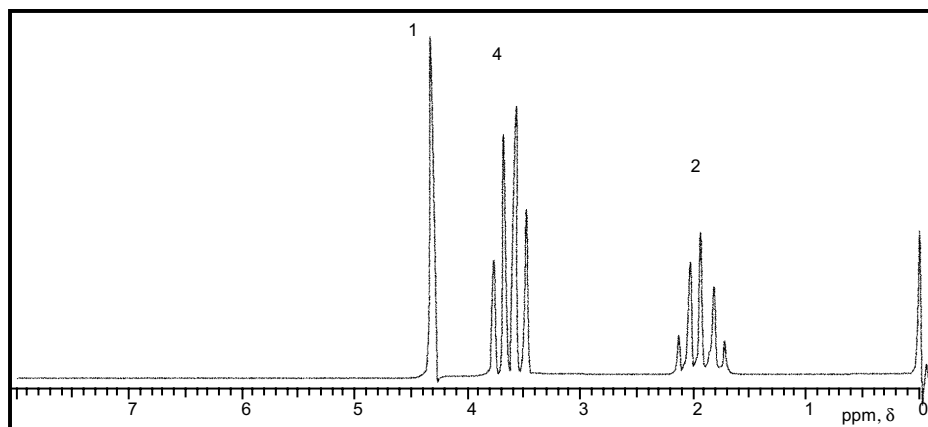


Compound 77 is a neutral liquid (boiling point 161° C) containing halogen. The peak at 3.85 ppm in the ^1H NMR disappears if the compound is exposed to D_2O . The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 38.52; H, 6.47; O, 17.11; contains halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

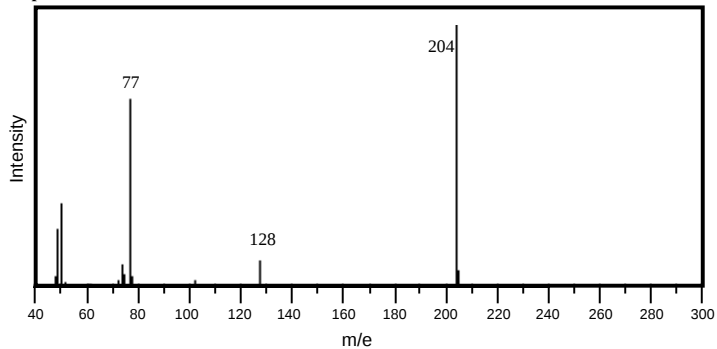
triplet, 63.5 ppm;
triplet, 44.1 ppm;
triplet, 41.7 ppm

Structure:

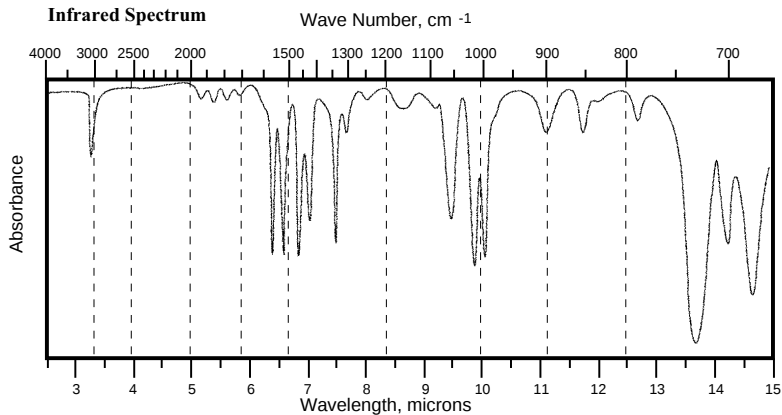
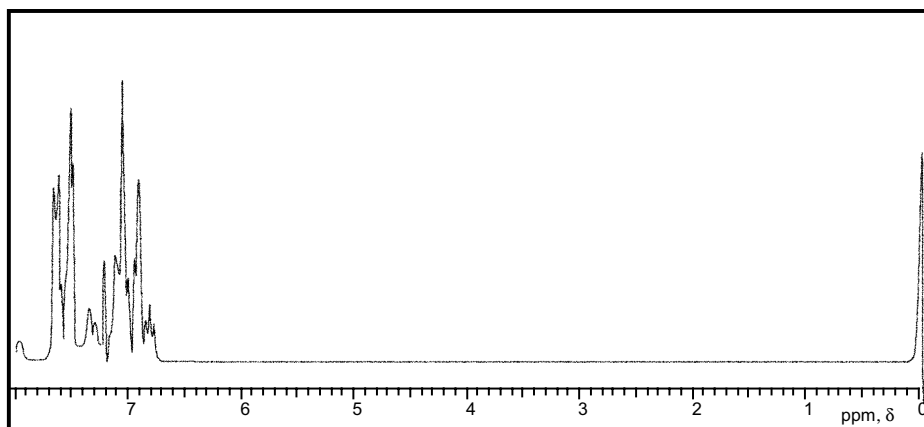


Compound 78 is a high-boiling liquid (boiling point 189° C) that contains halogen, but will not react with alkoxides to yield an ether. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 35.32; H, 2.47; contains halogen.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

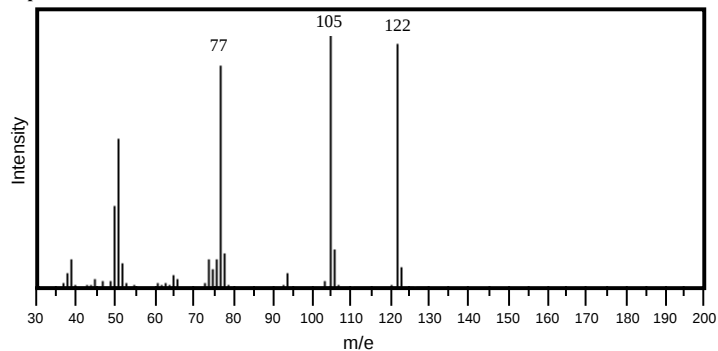
doublet, 137.4 ppm;
doublet, 130.1 ppm;
doublet, 127.4 ppm;
singlet, 97.3 ppm

Structure:

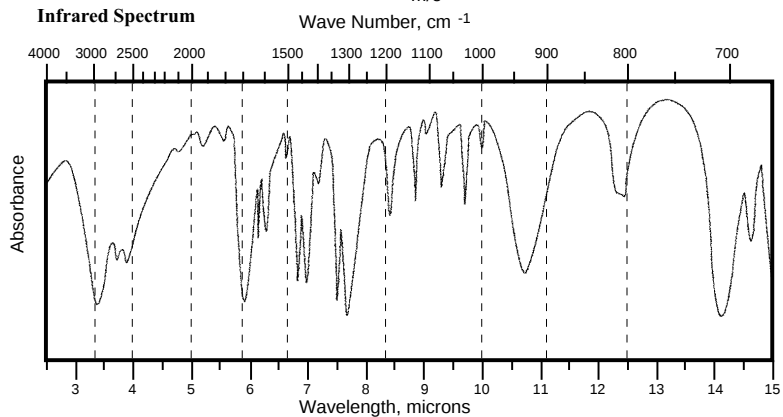
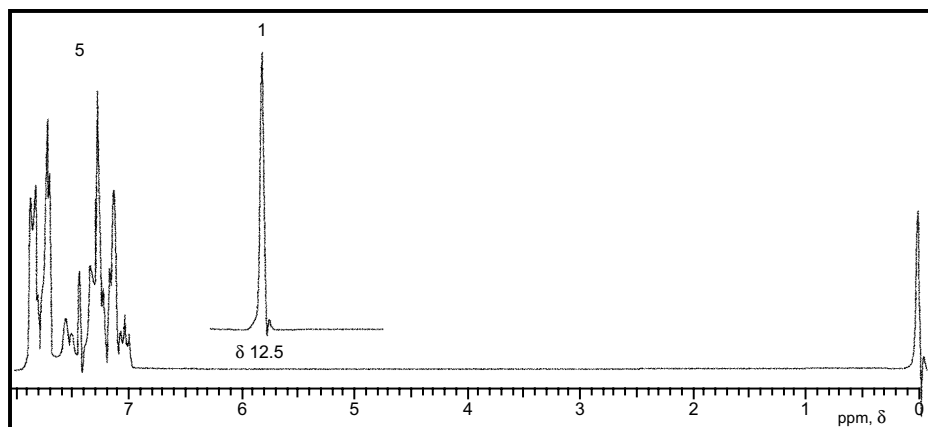


Compound 79 is a solid (melting point 122 ° C), that can be prepared by the oxidation of **Compound 13** with neutral KMnO_4 . The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 68.85; H, 4.95; O, 26.20.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

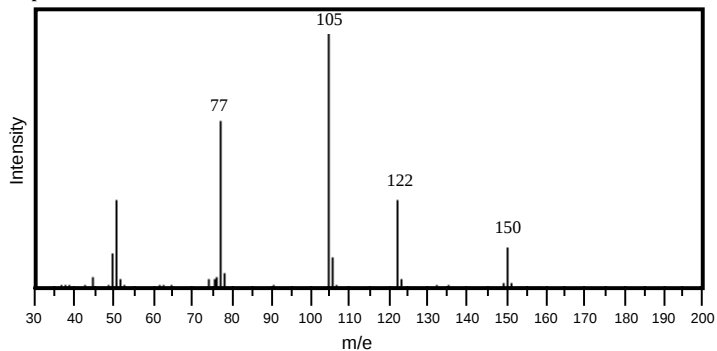
singlet, 172.0 ppm
 doublet, 133.7 ppm
 singlet, 130.6 ppm
 doublet, 130.1 ppm
 doublet, 128.4 ppm

Structure:

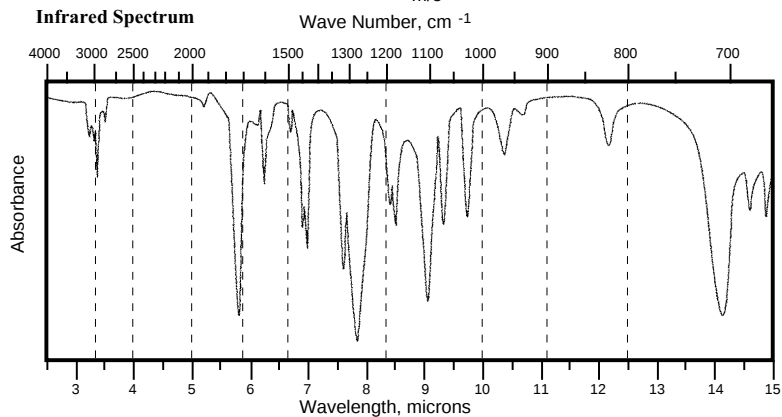
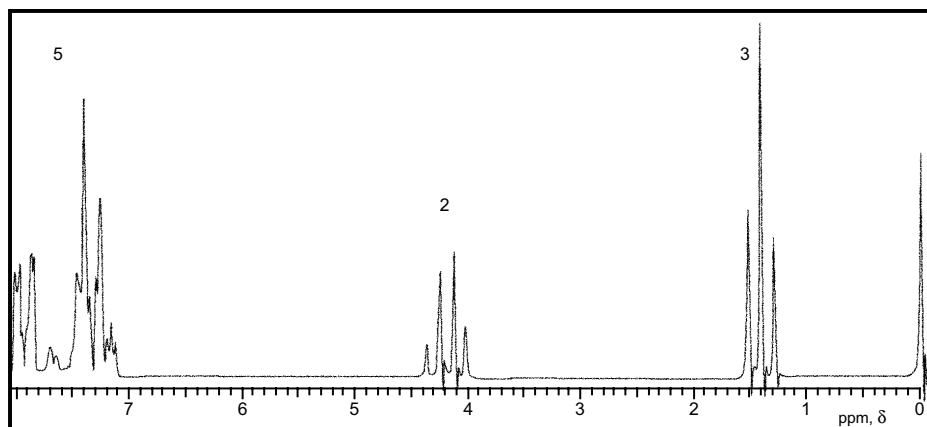


Compound 80 is a liquid (boiling point 212 ° C), that can be prepared by the reaction of **Compound 79** with acidic, anhydrous ethanol. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 71.98; H, 6.71; O, 21.31.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

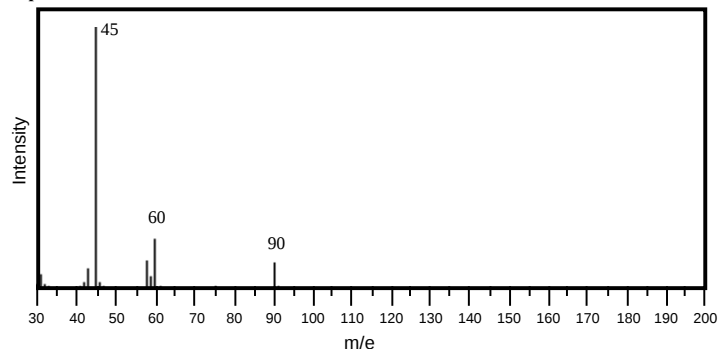
singlet, 167.0 ppm
 doublet, 132.8 ppm
 singlet, 130.5 ppm
 doublet, 129.7 ppm
 doublet, 128.4 ppm
 triplet, 59.1 ppm
 quartet, 13.6 ppm

Structure:

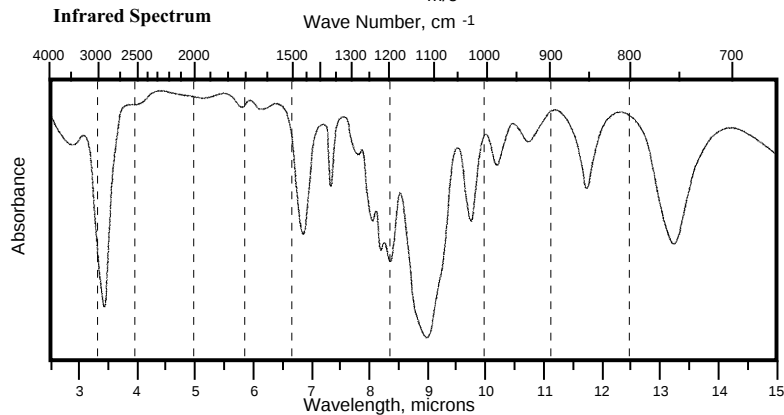
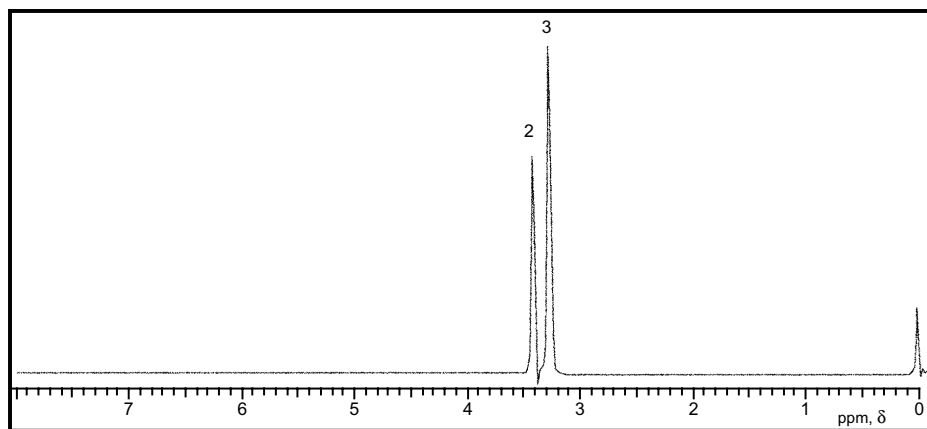


Compound 81 is a liquid (boiling point 85° C) that is commonly used as an aprotic solvent. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. The molecule has internal symmetry, which makes the ^1H NMR appear as two singlets, as shown. **Elemental Analysis:** C, 53.31; H, 11.18; O, 35.51.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

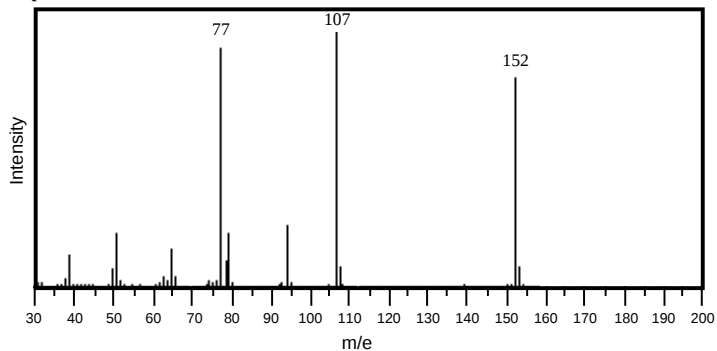
triplet, 79.6 ppm;
quartet, 53.9 ppm

Structure:

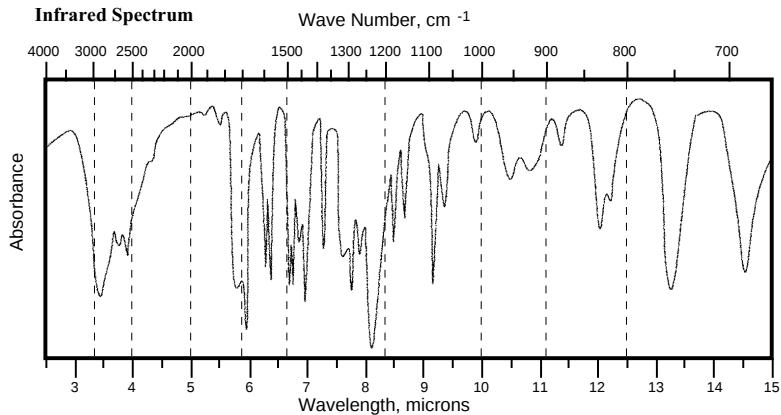
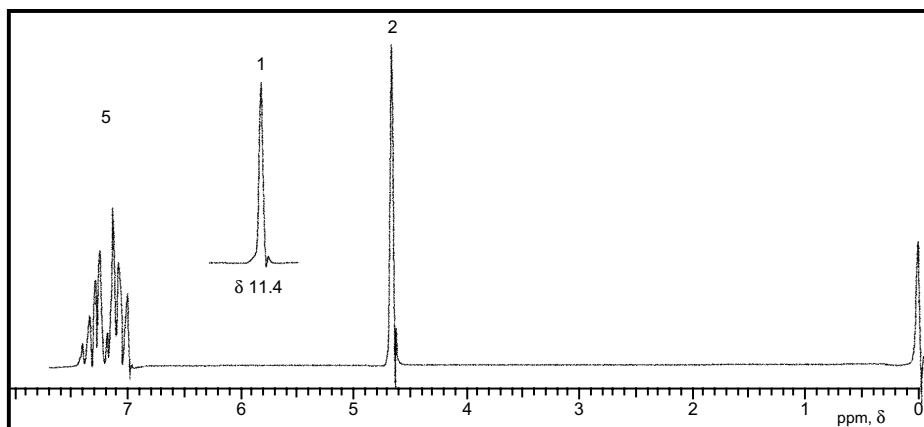


Compound 82 is a solid (melting point 98-100 ° C), that can be prepared by the reaction between the anion of **Compound 54** and iodoacetic acid. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 63.15; H, 5.30; O, 31.55.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

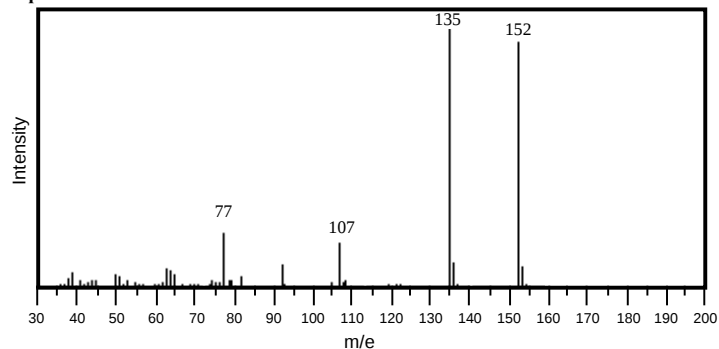
singlet, 176.0 ppm
singlet, 158.8 ppm
doublet, 129.1 ppm
doublet, 120.1 ppm
doublet, 114.2 ppm
triplet, 81.2 ppm

Structure:

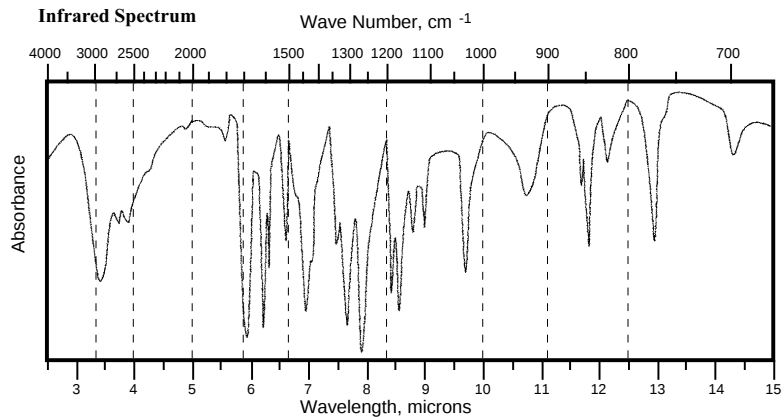
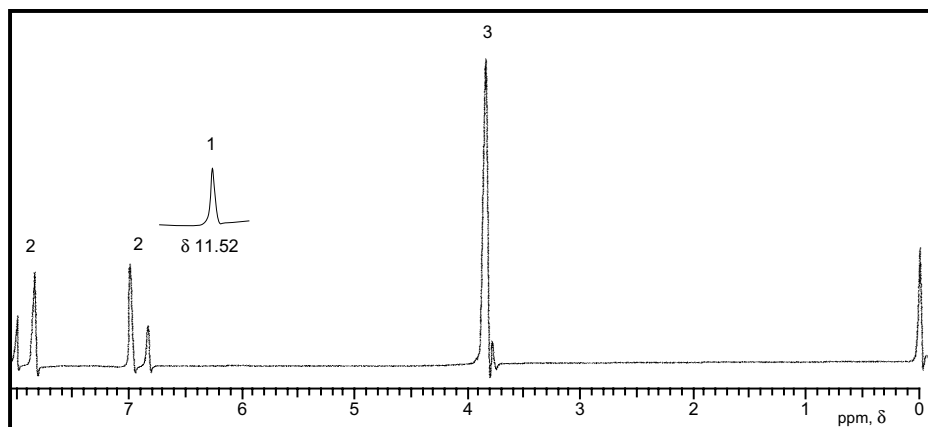


Compound 83 is a high-boiling liquid (boiling point 183 °C), that can be prepared by the oxidation of **Compound 44** with acidic KMnO_4 . The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 63.15; H, 5.30; O, 31.55.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

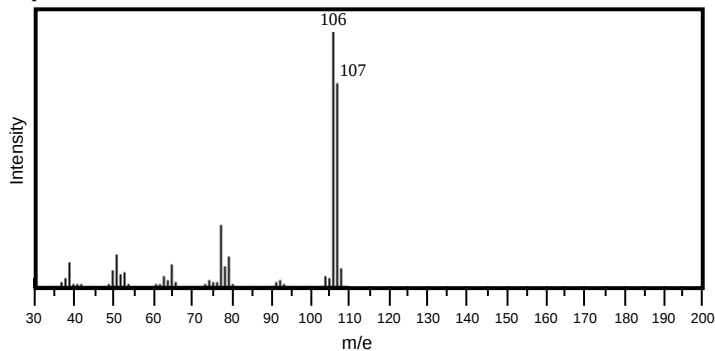
singlet, 172.0 ppm
singlet, 167.2 ppm
doublet, 131.1 ppm
singlet, 122.9 ppm
doublet, 114.0 ppm
quartet, 56.0 ppm

Structure:

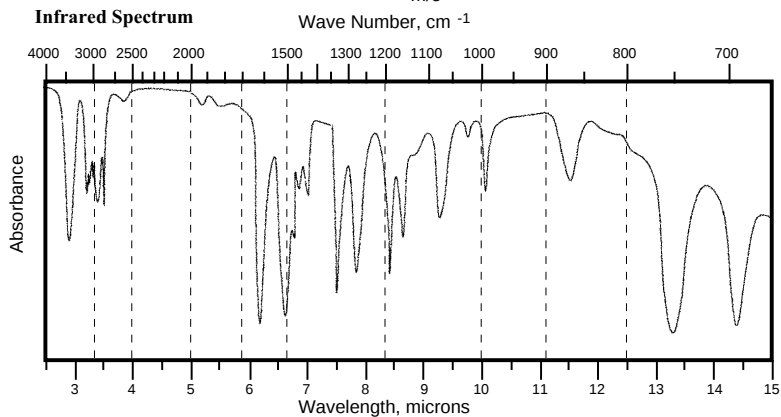
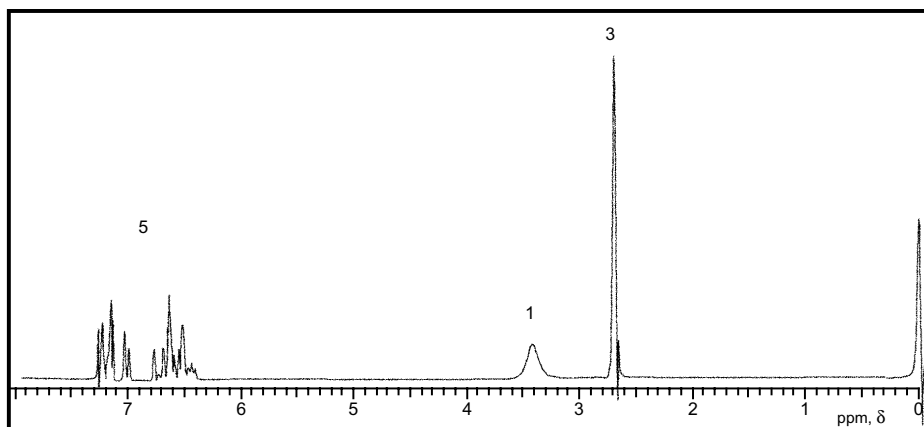


Compound 84 is a liquid (boiling point 81-82 °C @ 14 mm Hg), that reacts with *p*-toluenesulfonyl chloride to form a sulfonamide which is **not soluble** in strong base (this is the "Hindsburg test"). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 78.46; H, 8.47; N, 13.07.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

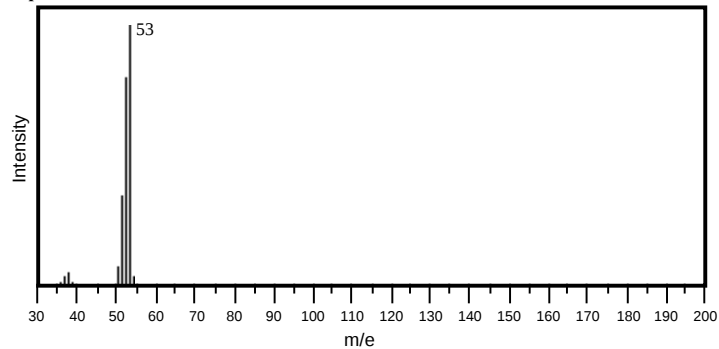
singlet, 143.5 ppm
 doublet, 129.3 ppm
 doublet, 116.9 ppm
 doublet, 112.3 ppm
 quartet, 40.3 ppm

Structure:

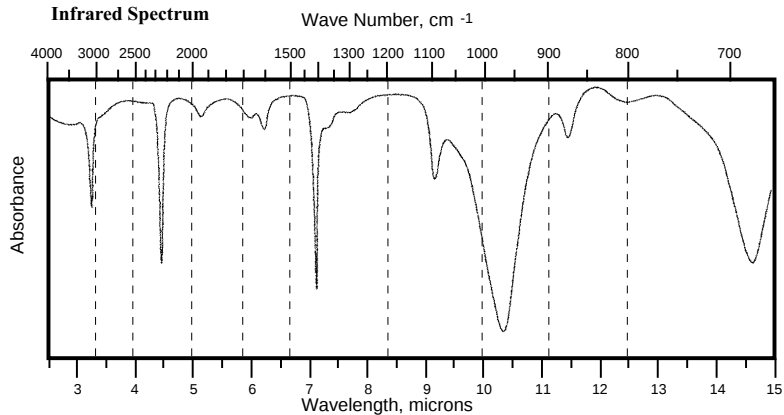
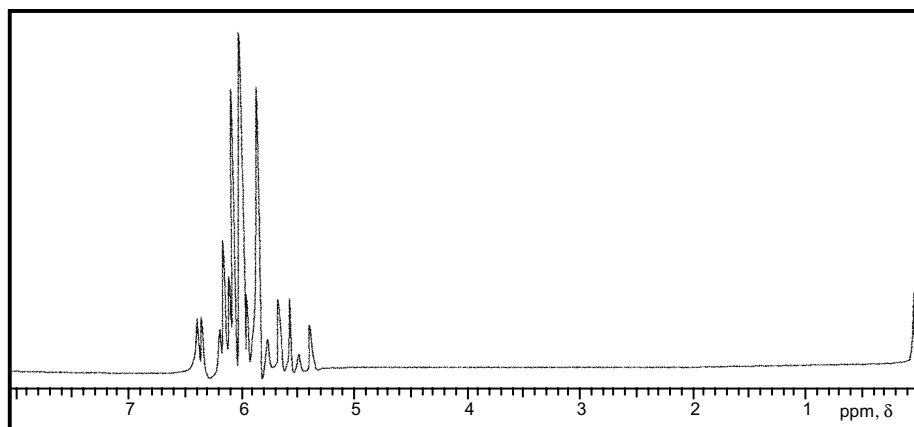


Compound 85 is a neutral liquid (boiling point 78° C) that readily undergoes conjugate addition reactions with amine nucleophiles. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 67.90; H, 5.70; N, 26.40.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

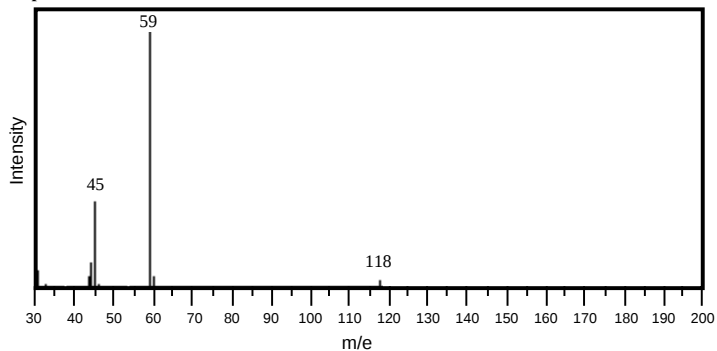
triplet, 137.5 ppm;
singlet, 117.2 ppm;
doublet, 106.2 ppm

Structure:

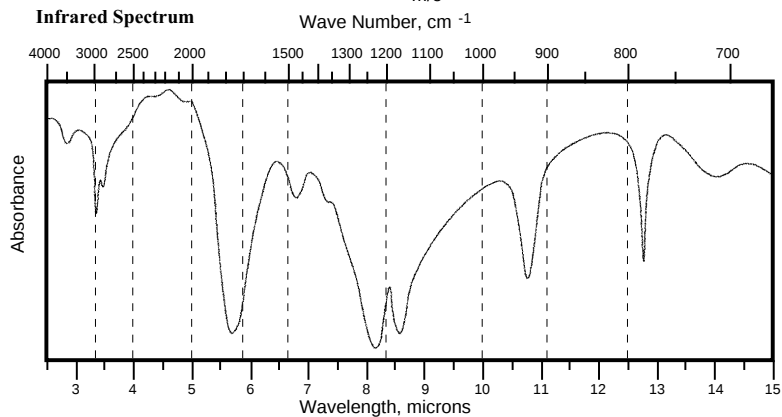
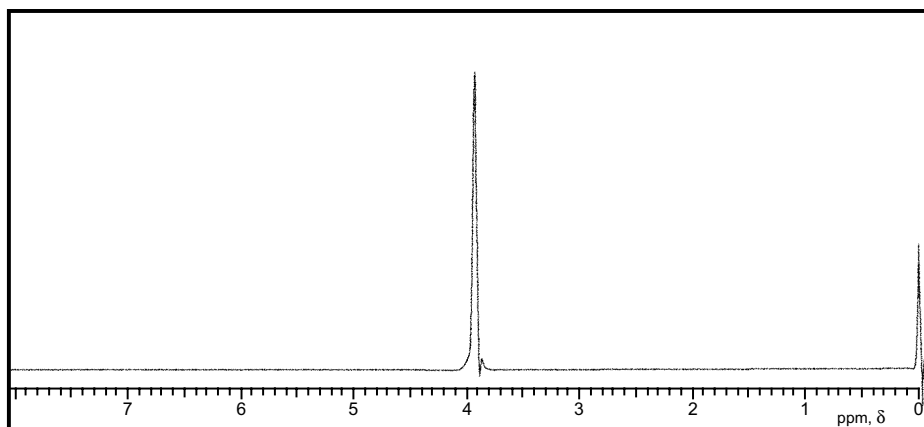


Compound 86 is a solid (melting point 50-54 °C), that has internal symmetry. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 40.68; H, 5.12; O, 54.19.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

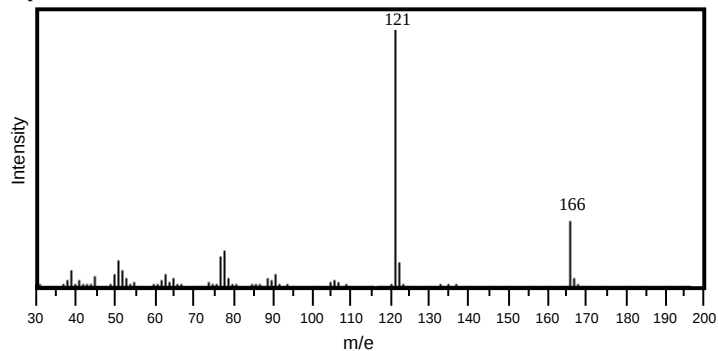
singlet, 155.9 ppm
quartet, 49.8 ppm

Structure:

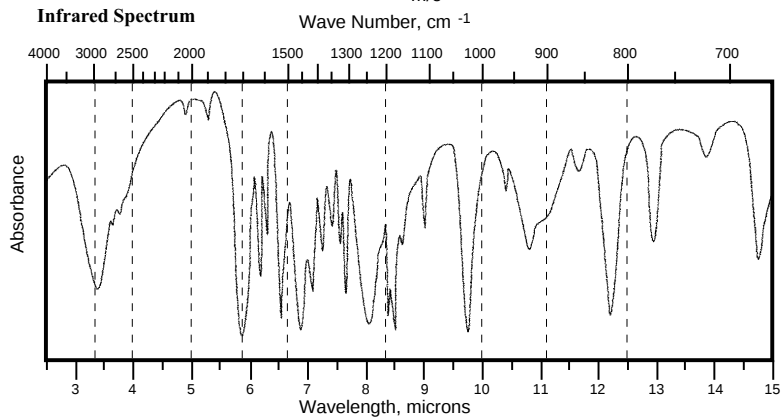
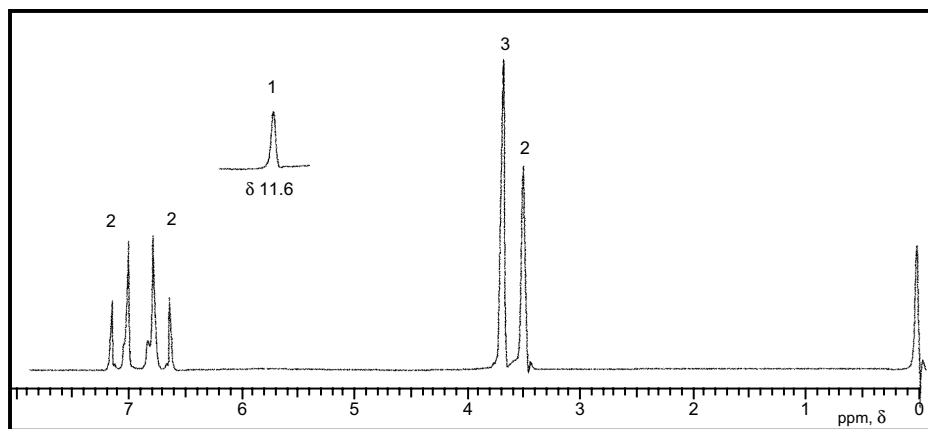


Compound 87 is a solid (melting point 86-88 °C), that is formed by treatment of **Compound 29** with I_2 in aqueous base, followed by acidification. The Mass, IR, and 1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 65.05; H, 6.07; O, 28.88.

Mass Spectrum



Infrared Spectrum

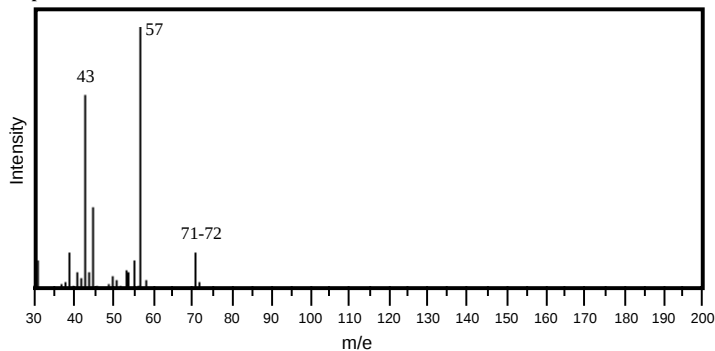
 1H NMR **^{13}C Spectral Data:**

singlet, 178.0 ppm
 singlet, 160.8 ppm
 doublet, 130.9 ppm
 singlet, 127.3 ppm
 doublet, 114.5 ppm
 quartet, 56.0 ppm
 triplet, 43.8 ppm

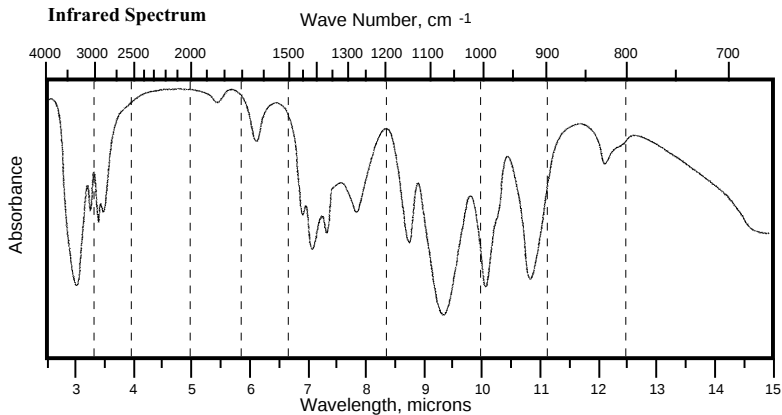
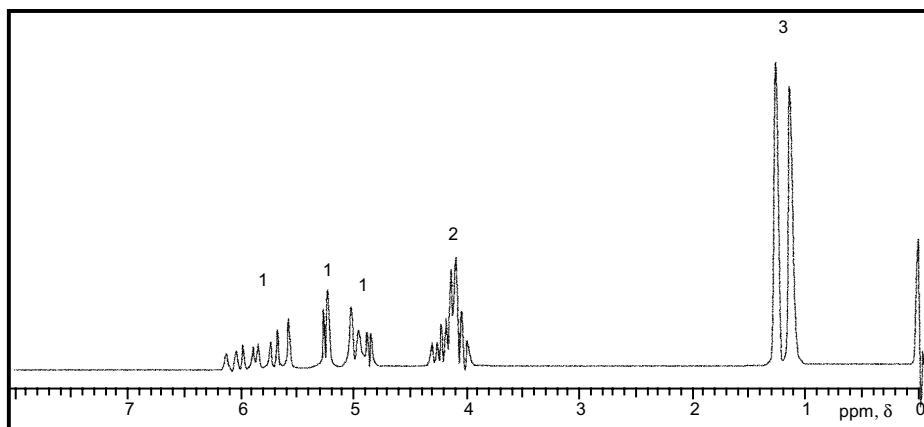
Structure:

Compound 88 is a liquid (boiling point 97° C), that reacts with bromine to give a 1,2-dibromide. The integration of the multiplet at 4.1 ppm in the ^1H NMR changes from 2 to 1 if the compound is exposed to D_2O . The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 66.63; H, 11.18; O, 22.19.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

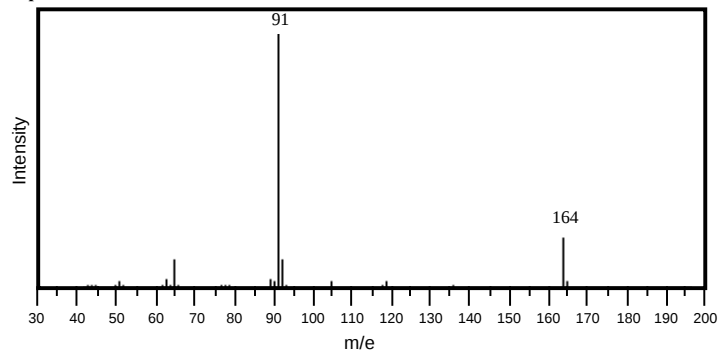
doublet, 137.5 ppm;
triplet, 115.1 ppm;
doublet, 77.8 ppm;
quartet, 23.8 ppm

Structure:

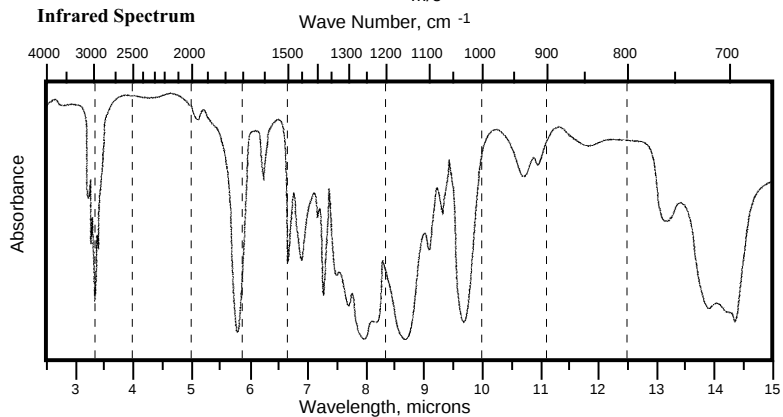
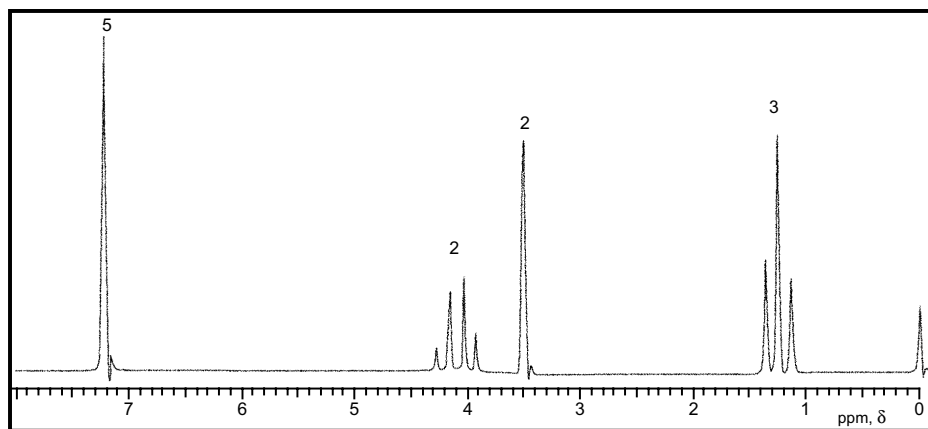


Compound 89 is a liquid (boiling point 229 ° C), that can be formed by the reaction of **Compound 37** with acidic, anhydrous ethanol. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 73.15; H, 7.37; O,

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

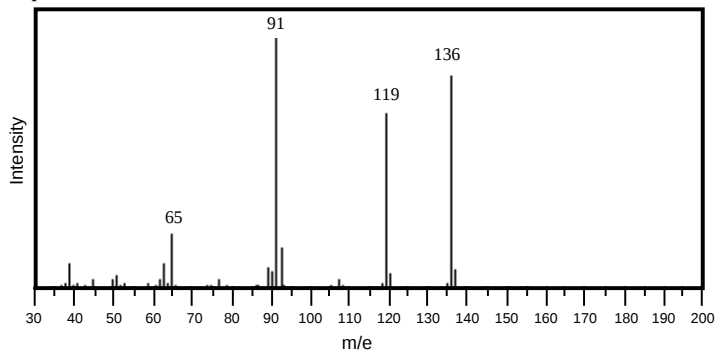
singlet, 173.0 ppm
singlet, 135.0 ppm
doublet, 129.9 ppm
doublet, 128.9 ppm
doublet, 127.3 ppm
triplet, 59.5 ppm
triplet, 41.6 ppm
quartet, 13.6 ppm

Structure:

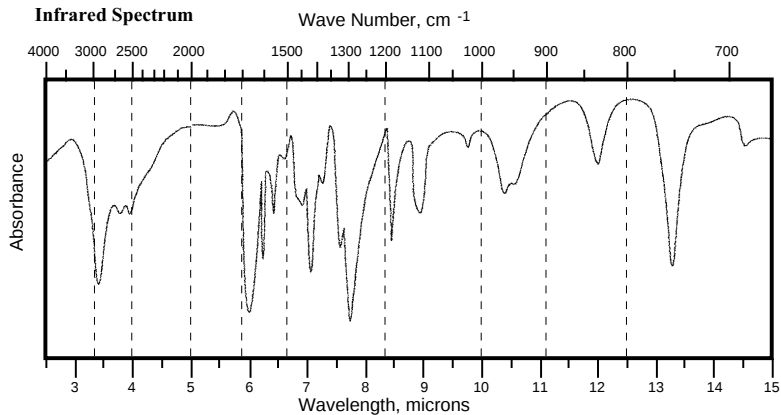
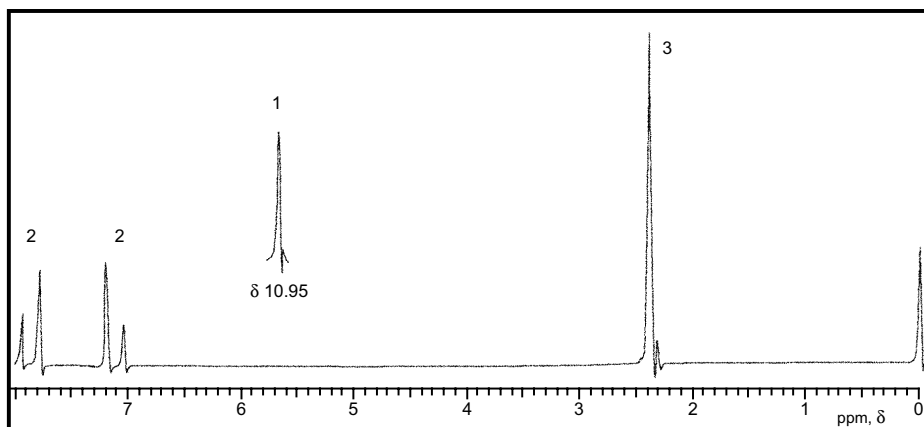


Compound 90 is a solid (melting point 180-182 ° C), that can be formed by the hydrolysis of **Compound 20** in strong acid. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 70.57; H, 5.92; O, 23.50.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

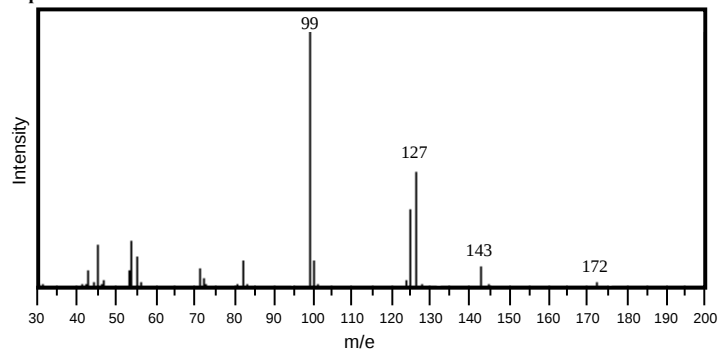
singlet, 172.0 ppm
singlet, 142.9 ppm
doublet, 130.0 ppm
doublet, 129.1 ppm
singlet, 127.6 ppm
quartet, 22.0 ppm

Structure:

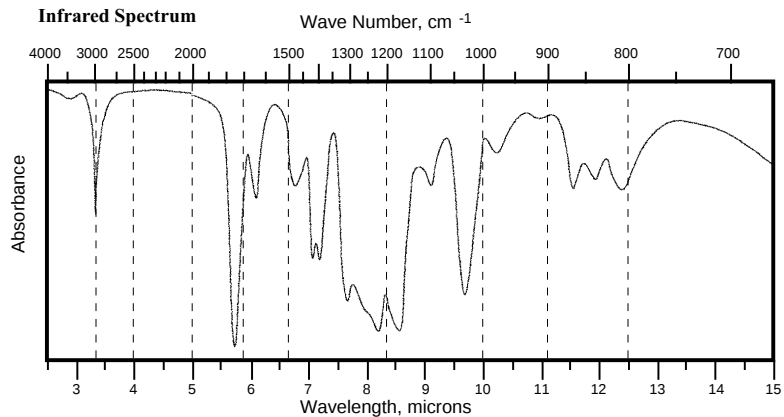
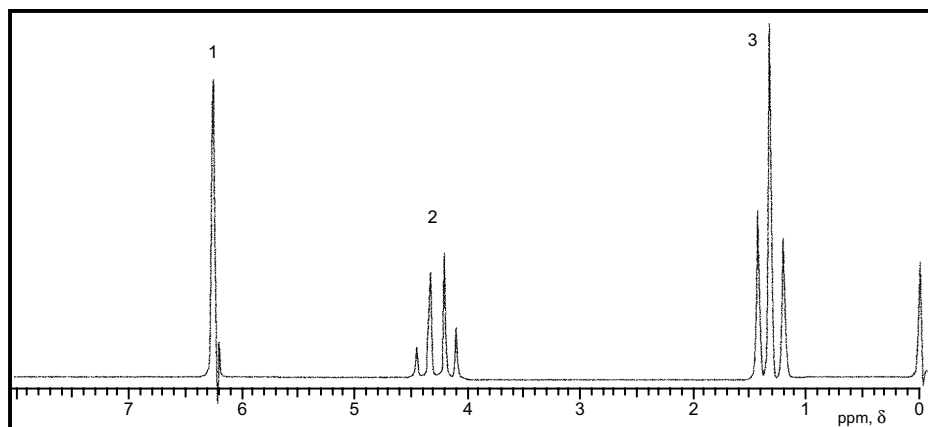


Compound 91 is a liquid (boiling point 225 ° C). Hydrolysis of the compound in aqueous acid, followed by heating of the solid product results in the loss of water and the formation of a cyclic carboxylic acid anhydride. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 55.81; H, 7.02; O, 37.17.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

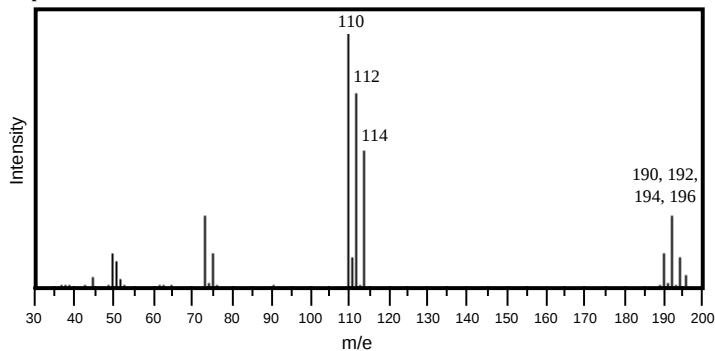
singlet, 165.0 ppm
doublet, 135.6 ppm
triplet, 59.6 ppm
quartet, 13.7 ppm

Structure:

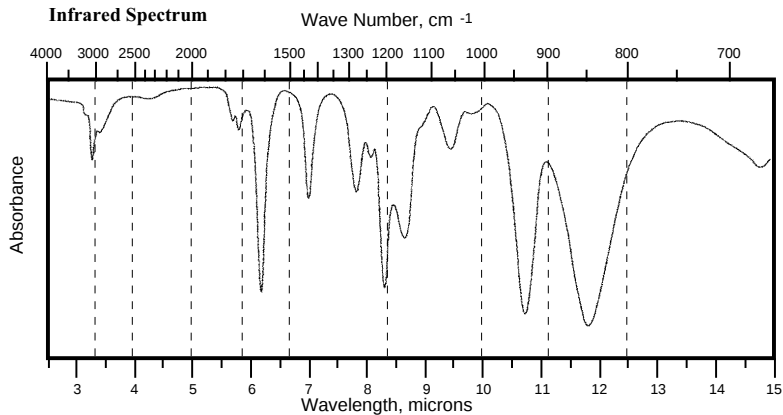
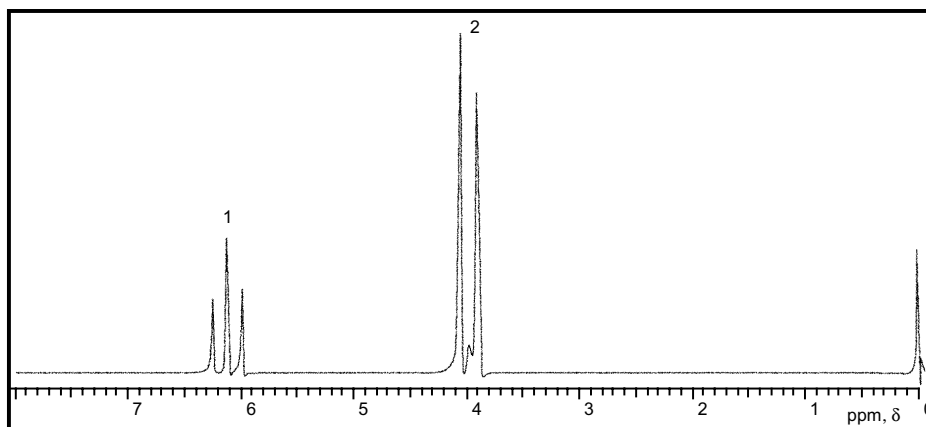


Compound 92 is a liquid which contains two different halogens; **E - Z** nomenclature is not applicable to this isomer. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 18.98; H, 1.59; contains two moles of one halogen, and one mole of a second.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

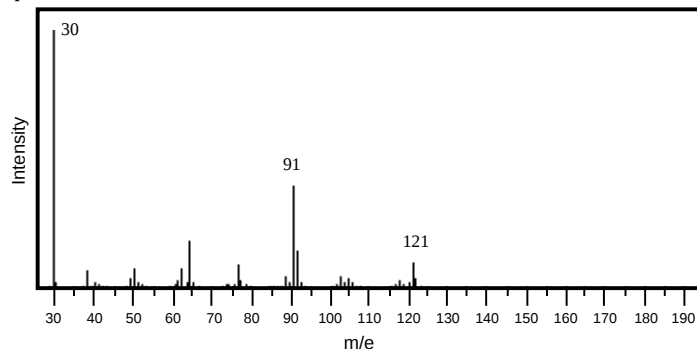
singlet, 157.1 ppm;
doublet, 81.3 ppm;
triplet, 18.7 ppm

Structure:

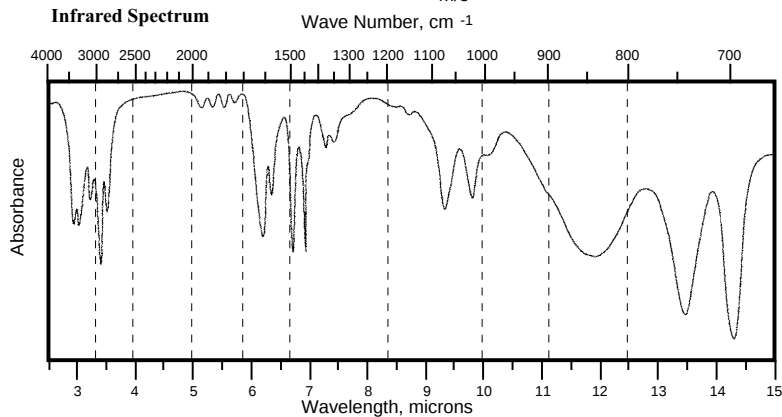
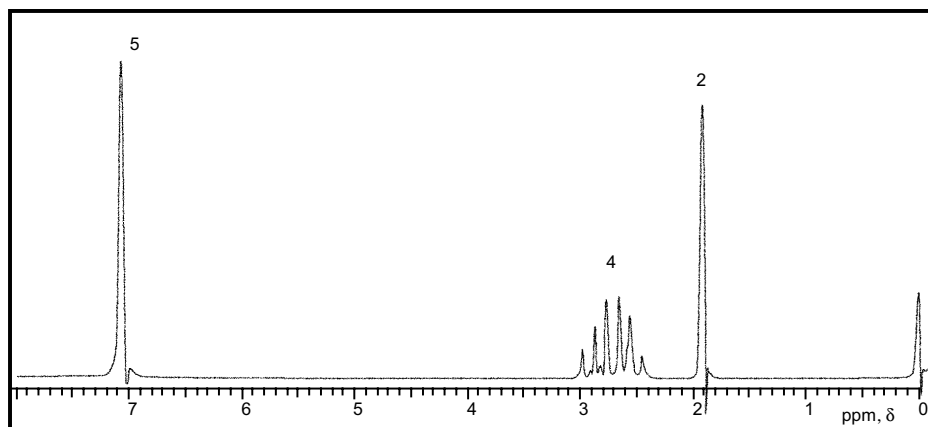


Compound 93 is a high-boiling basic liquid (boiling point 195° C). The peak at 0.9 ppm in the ^1H NMR disappears if the compound is exposed to D_2O . The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 79.29; H, 9.15; N, 11.56.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

singlet, 140.2 ppm;
doublet, 128.4 ppm;
doublet, 127.9 ppm;
doublet, 125.7 ppm;
triplet, 47.8 ppm;
triplet, 45.8 ppm

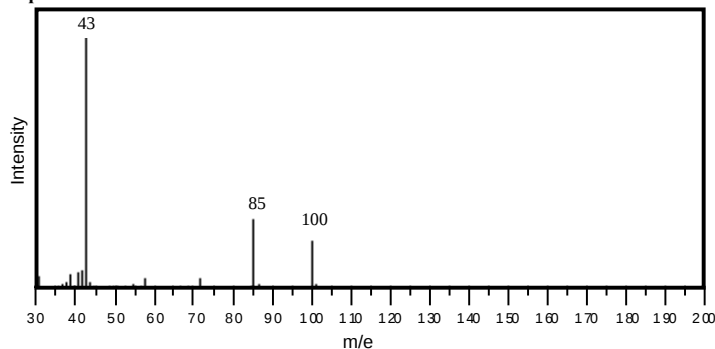
Structure:



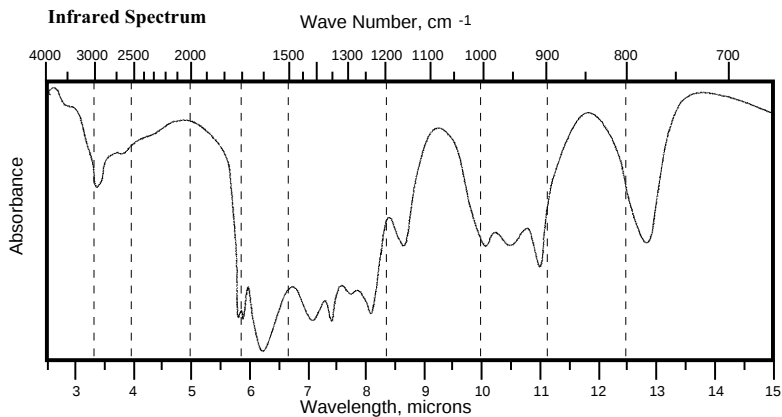
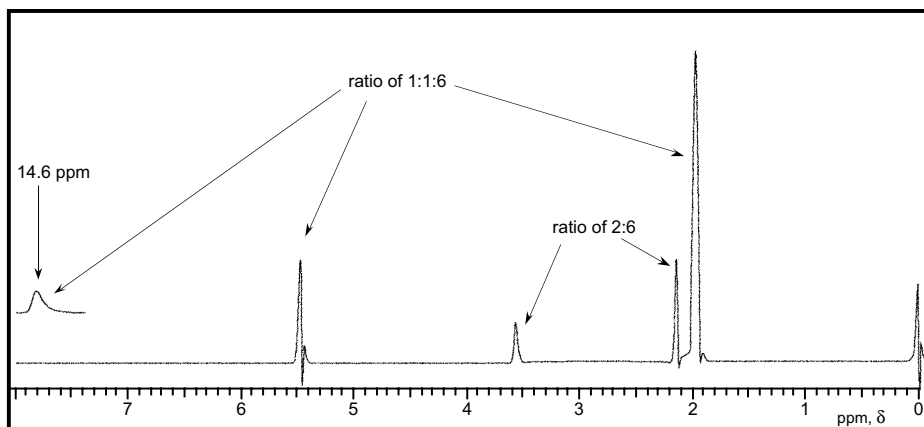
Compound 94 is a liquid (boiling point 140° C) that reacts with I_2 in aqueous base to give a yellow precipitate of CHI_3 (the iodoform test). The Mass, IR, and 1H NMR spectra, along with ^{13}C NMR data, are given below. The 1H NMR spectrum shows the parent compound in equilibrium with a major tautomeric isomer and the peaks corresponding to both forms are indicated on the spectrum.

Elemental Analysis: C, 59.98; H, 8.05; O, 31.96.

Mass Spectrum



Infrared Spectrum

 1H NMR ^{13}C Spectral Data:

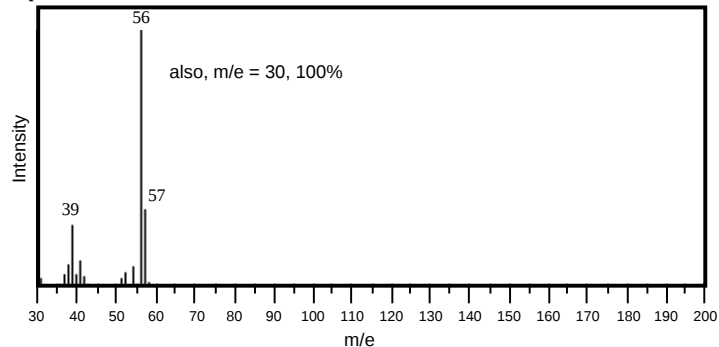
singlet, 207.1 ppm;
triplet, 56.3 ppm;
quartet, 24.3 ppm
(data for keto
tautomer)

Structure:

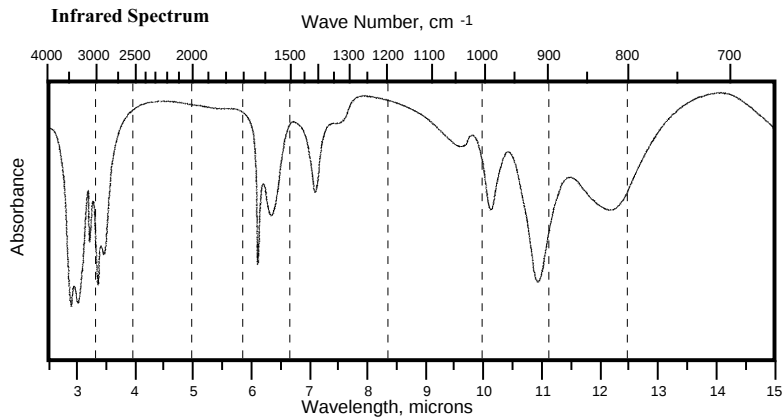
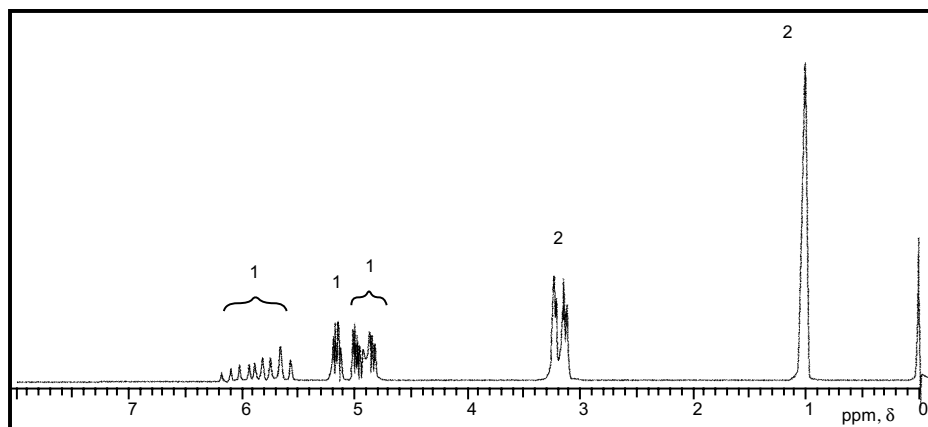


Compound 95 is a foul-smelling basic liquid (boiling point 53° C), that reacts with bromine in CCl₄ to yield a 1,2-dibromide. The Mass, IR, and ¹H NMR spectra, along with ¹³C NMR data, are given below. **Elemental Analysis:** C, 63.11; H, 12.36; N, 24.53.

Mass Spectrum



Infrared Spectrum

¹H NMR¹³C Spectral Data:

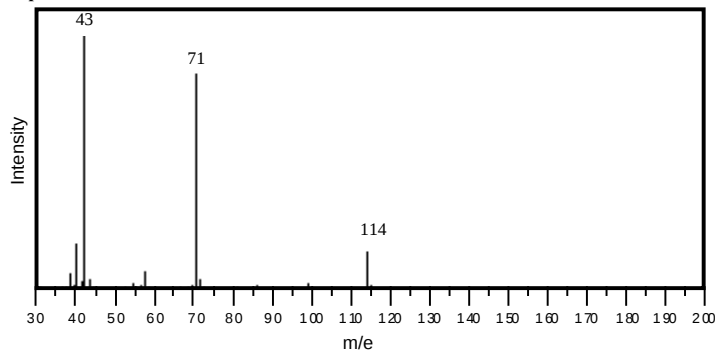
doublet, 134.3 ppm;
triplet, 114.9 ppm;
triplet, 48.9 ppm

Structure:

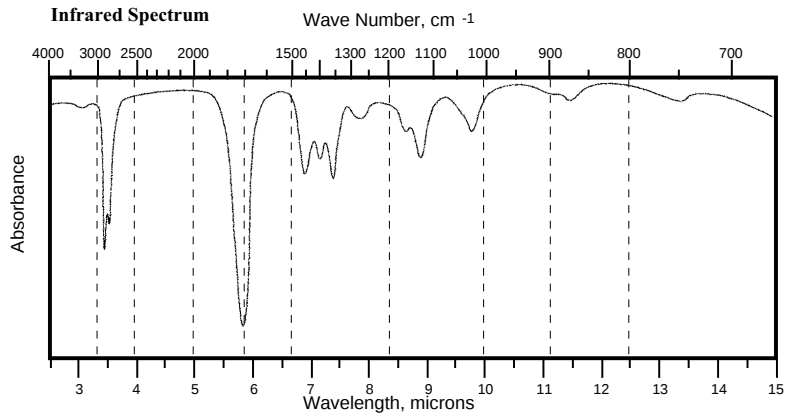
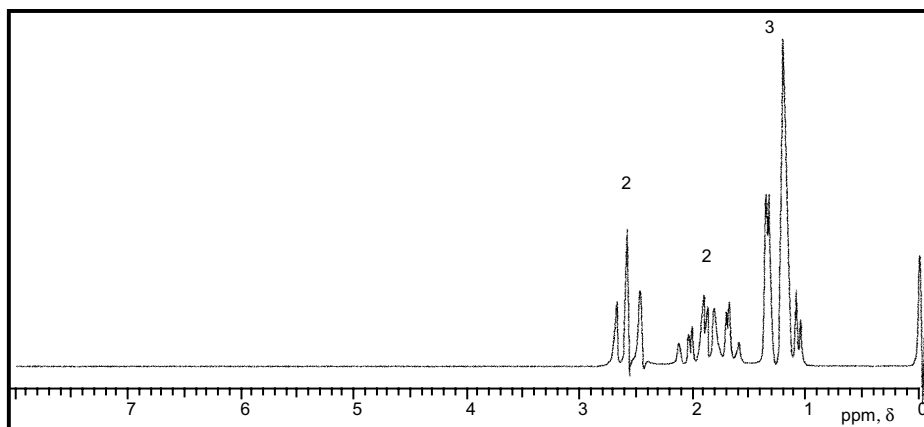


Compound 96 is a liquid (boiling point 144° C) that gives a yellow precipitate with 2,4-dinitrophenylhydrazine reagent, but does not react with I_2 in aqueous base to give a yellow precipitate of CHI_3 (a negative iodoform test). The compound can be formed by the condensation of two moles of ethyl butanoate in ethoxide/ethanol, followed by acidification and heating. The Mass, IR, and 1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 73.63; H, 12.36; O, 14.01.

Mass Spectrum



Infrared Spectrum

 1H NMR ^{13}C Spectral Data:

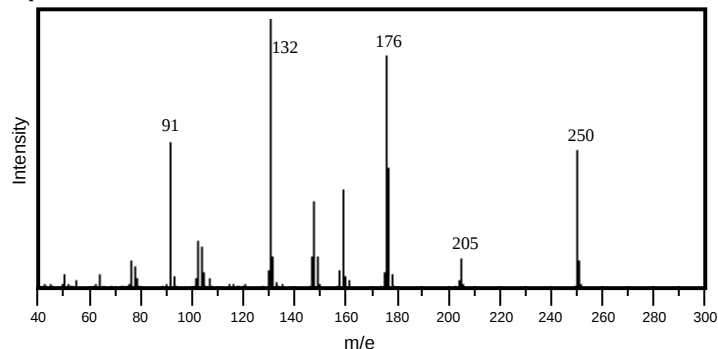
singlet, 208.2 ppm;
triplet, 46.7 ppm;
triplet, 20.1 ppm;
quartet, 13.5 ppm

Structure:

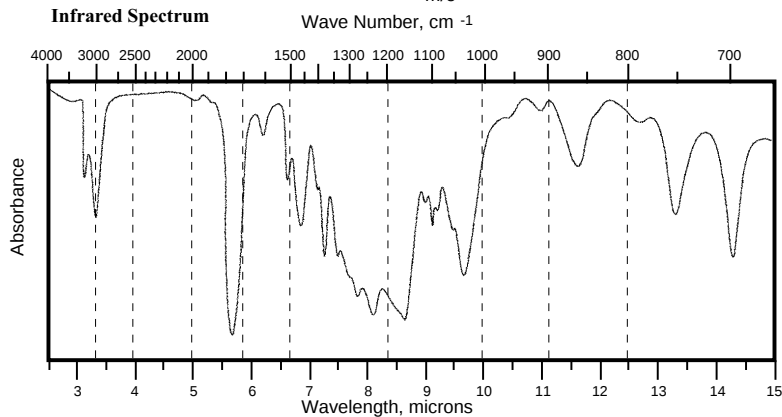
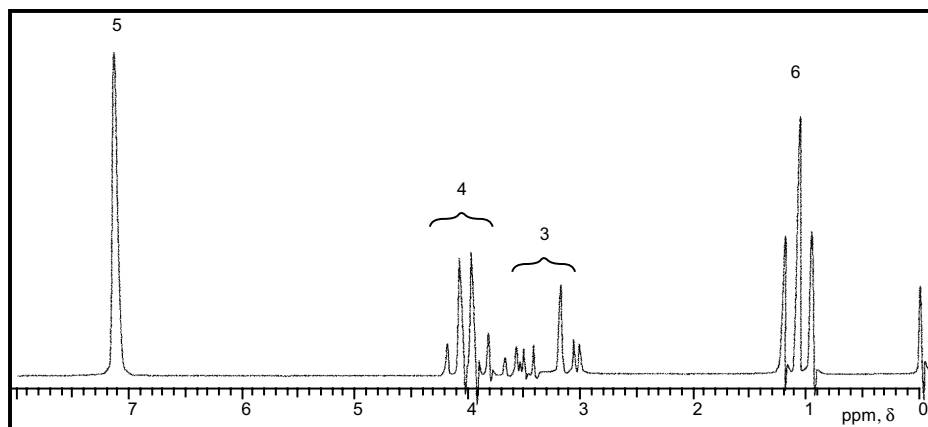


Compound 97 is a high-boiling liquid (boiling point 301 °C) that can be formed by the reaction of **Compound 75** with **Compound 9** in the presence of alkoxide. The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 67.18; H, 7.25; O, 25.57.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

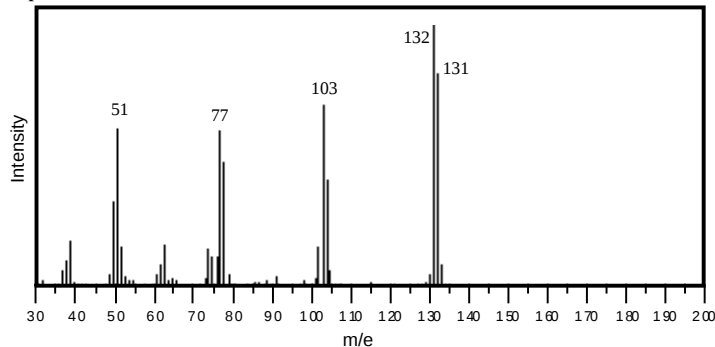
singlet, 174.5 ppm;
singlet, 141.1 ppm;
doublet, 128.7 ppm;
doublet, 127.6 ppm;
doublet, 125.3 ppm;
triplet, 59.5 ppm;
doublet, 57.8 ppm;
triplet, 35.7 ppm;
quartet, 13.6 ppm

Structure:

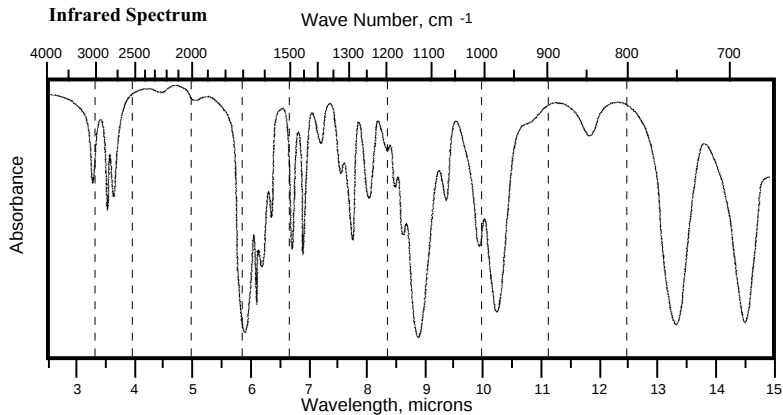
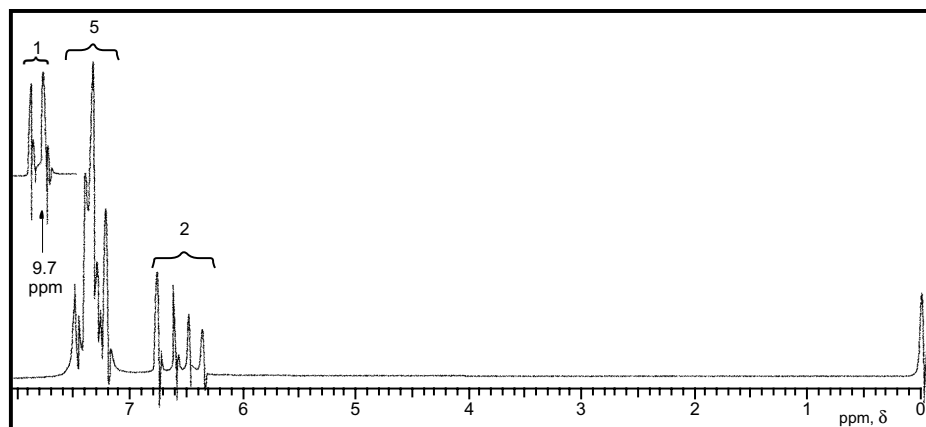


Compound 98 is a liquid (boiling point 251° C) that can be prepared by a mixed aldol condensation, followed by acid-catalyzed dehydration. The compound reacts with Ag^+ ion in aqueous ammonia to form a "silver mirror" (the Tollens test). The Mass, IR, and ^1H NMR spectra, along with ^{13}C NMR data, are given below; the stereochemistry can be deduced from the coupling constants in the region around 6.5 ppm ($J \approx 16$ Hz). **Elemental Analysis:** C, 81.79; H, 6.10; O, 12.11.

Mass Spectrum



Infrared Spectrum

 ^1H NMR ^{13}C Spectral Data:

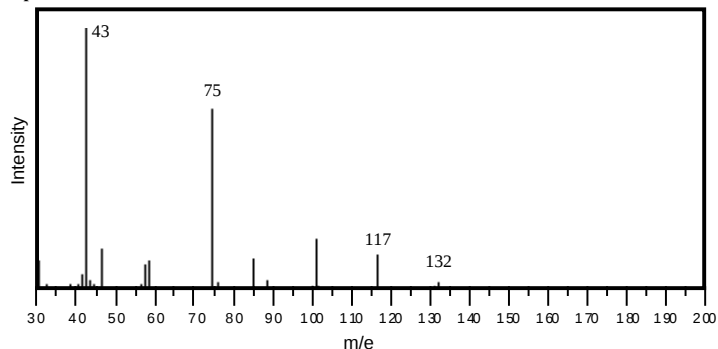
doublet, 190.0 ppm;
doublet, 150.3 ppm;
singlet, 134.9 ppm;
doublet, 129.6 ppm;
doublet, 128.4 ppm;
doublet, 127.7 ppm;
doublet, 126.2 ppm

Structure:

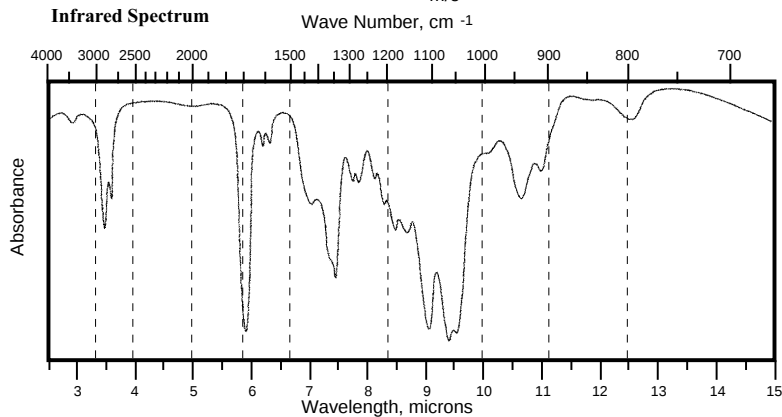
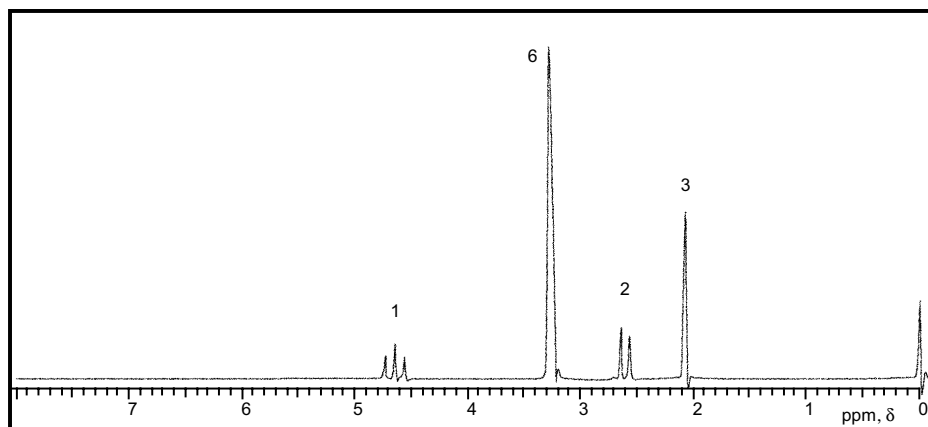


Compound 99 is a high-boiling liquid that reacts with I_2 in aqueous base to give a yellow precipitate of CHI_3 (the iodoform test). The compound itself does not react with Ag^+ ion in aqueous ammonia to form a “silver mirror” (a negative Tollens test); however, if the compound is first acidified in aqueous solution and then tested, a positive Tollens test is observed. The Mass, IR, and 1H NMR spectra, along with ^{13}C NMR data, are given below. **Elemental Analysis:** C, 54.53; H, 9.15; O, 36.32.

Mass Spectrum



Infrared Spectrum

 1H NMR ^{13}C Spectral Data:

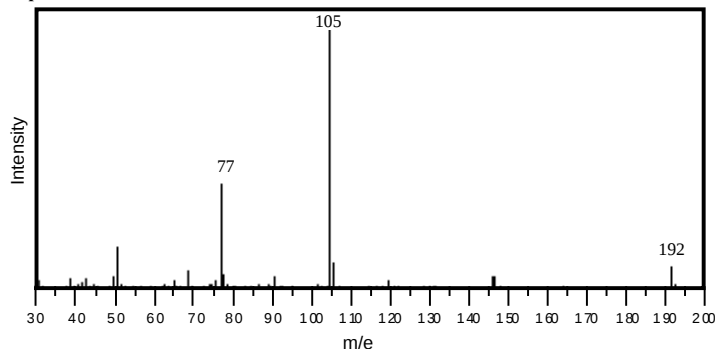
singlet, 207.1 ppm;
doublet, 117.9 ppm;
triplet, 51.3 ppm;
quartet, 47.7 ppm;
quartet, 25.1 ppm

Structure:

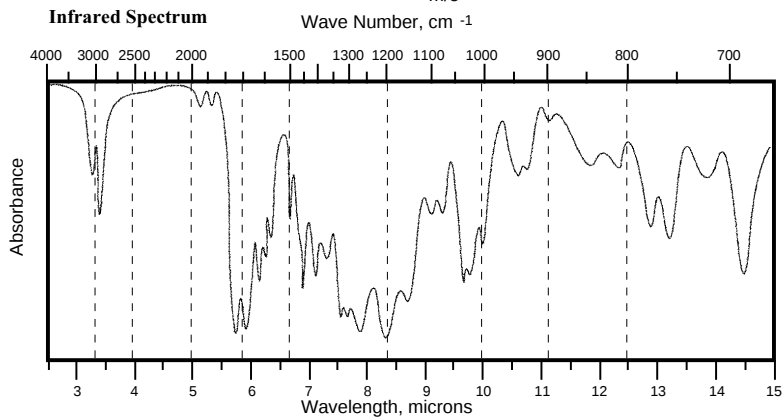
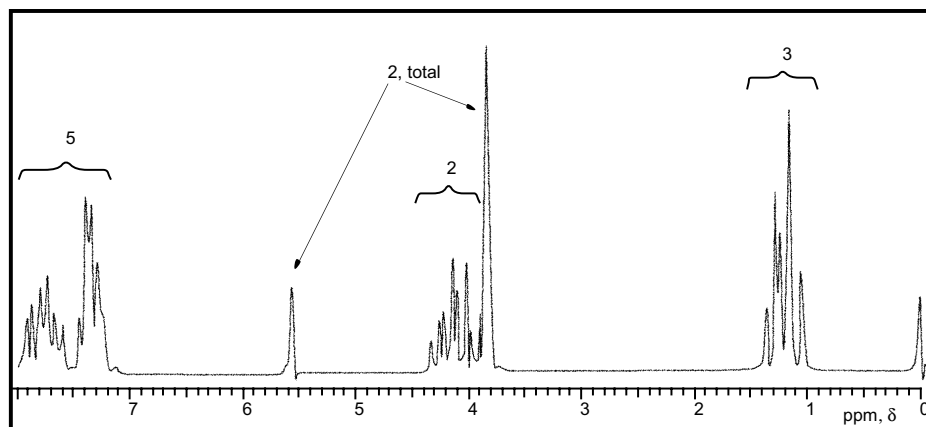


Compound 100 is a high-boiling liquid (boiling point 265° C) that does not react with I_2 in aqueous base to give a yellow precipitate of CHI_3 (a negative iodoform test). The Mass, IR, and 1H NMR spectra, along with ^{13}C NMR data, are given below. The 1H NMR spectrum shows the parent compound in equilibrium with a major tautomeric isomer. Use the total integrations and the chemical shifts of the major peaks to determine the structure of the major tautomer. **Elemental Analysis:** C, 68.74; H, 6.29; O, 24.97.

Mass Spectrum



Infrared Spectrum

 1H NMR ^{13}C Spectral Data:

singlet, 197.6 ppm;
 singlet, 172.0 ppm;
 singlet, 137.4 ppm;
 doublet, 132.9 ppm;
 doublet, 128.6 ppm;
 doublet, 128.4 ppm;
 triplet, 59.2 ppm;
 triplet, 46.6 ppm;
 quartet, 13.6 ppm

Structure:

